The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume III DECEMBER, 1911 No. 12

Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly.
Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

EDITORIALS

PROFESSIONAL ETIQUETTE.

At a time when our Society is endeavoring to obtain from the Federal, State and Municipal Governments that recognition to which it is entitled by virtue of its aims, its size and the representative men of science who are included in its membership, it seems most desirable and necessary that some consideration be given the subject of Professional Etiquette. An early discussion of this subject appears to be almost mandatory if the public at large is to place in a chemist's opinion that confidence which it now places in *the opinions* of physicians and lawyers. The two last-named professions are held up to a certain standard by the State Examining Boards for law and medicine, and this preliminary process of elimination is in a certain sense followed up by the supervision of various county medical societies and bar associations. It may be that we will in the future have state examinations for food chemists, sanitary chemists and municipal chemists, but at this writing there is nothing that will assure the layman that a certain man has enjoyed that necessary education which properly fits him for making accurate analyses and rendering opinions on matters involving chemical principles. At the present time it quite frequently happens that a manufacturer submits a commercial product to "one chemist after another" until he has three or more entirely different reports on the same article. It is this very fact, which is undermining the reputation of the chemical profession at large, and the importance of the subject warrants a careful consideration of the conditions.

About one year ago a specimen of bleached cotton was handed to the writer with the request that it be examined for chlorin. On returning a negative report, the bleacher stated that two other chemists had each found chlorin in the goods. A careful "following up" of the case showed that the two former chemists had examined for chlorides while the third chemist had examined for free chlorin which in this case was the only form of chlorin in which the bleacher was interested and which might prove dangerous. Thus it is seen that *incomplete* reports are as dangerous as careless analyses. Aside from these questions which involve foresight, accuracy and perspective, we have many of us experienced public criticism (by chemists) of the work of other chemists. This has been resorted to, probably because the critic saw no other way of having a careless or less experienced colleague brought to task for having injured the standing of his profession. This in turn suggests to our minds the necessity of a Supervisory Board as a part of our American Chemical Society: a Board whose duty it shall be to hear complaints of members in cases involving a breach of professional etiquette or cases where the quality of the work done by a member reflects on the reputation of chemists as a *professional* body. Our Society should in no wise seek to dictate to the schools where a man obtains his chemical education but it should endeavor to define rather clearly the term "chemist," so that a manufacturer when seeking the advice of a chemist may obtain from the office of the American Chemical Society the name of a qualified chemist in any one of the important cities of our Country. If found advisable this list might be subdivided under such headings as Analysts, Engineering Chemists, Consulting Chemists (inorganic), Consulting Chemists (organic), etc.

Very recently the following incident was brought to the attention of the writer: "A," who is a consulting chemist, gave to "B," an analyst, and to "C," an analyst (both of these being reputable analytical chemists), a certain material which was to be examined qualitatively for the presence of arsenic. "B" reported that arsenic was absent while "C" reported the presence of a *considerable* amount of arsenic. "C" was corroborated in his report by "D" (another analyst). What credence is to be given the report of "B"? If "B's" methods are faulty, what is to warn a manufacturer of this fact? What redress has "A" if the report of "C" and "D" should prove inaccurate and needless anxiety has been caused by this fact?

To conclude, if the title of chemist, analyst, and so on, is given by the American Chemical Society to those of its members who possess definite qualifications, the manufacturers of our Country will cease to remark that "chemists are bluffers" as one gentleman recently put it in a private conversation. In other words, it is a *pleasure* to have one's name recorded as a member of our Society, but it should be an *honor* to be recognized as a qualified consulting chemist or analyst by the American Chemical Society.

FREDERIC DANNERTH.

THE POTASH SUPPLY.

There will always be a "potash situation" and the possibility of a controversy so long as the world's supply of potash happens to be lodged in one country and is controlled by a monopolistic combine of which the government of the country in question through its ownership of mines is a part. At the bottom of the recent and present controversy between the American consumers of potash and the German producers stands the fundamental fact that we are forced to buy our potash of Germany because there is no other source of supply. Germany can charge all that the trade will stand, for her potash, in defiance of any natural laws of supply and demand and Americans will have to pay the price.

The general situation has changed but little during the year and indeed not much change was expected after the failure of our government to reach a successful conclusion in its diplomatic negotiations. The American contractors, who arranged for the delivery of their requirements through an American concern which had in turn contracted with the independent mines, are paying syndicate prices for their deliveries, although the money is paid under protest on account of the sur-tax, and it is possible that some settlement will later be arrived at.

The great hope of American consumers lies in the discovery of adequate potash deposits in the United States. The government has wisely appropriated a sum of money, for the purpose of prospecting and investigating probable sources of supply. Recently announcement has been made by the Secretary of Agriculture that potash has been discovered in the West in large quantities, but details are withheld until the assembling of the next Congress, when they will be communicated to the legislative committees which have the matter in charge. It is to be hoped that this important announcement will be fully supported by the facts when they are made known and that the deposits will prove commercially available in the near future. No other influence, it would seem, can change the monopolistic German attitude.

The German Syndicate is already greatly interested in Secretary Wilson's announcement, and it has been pointed out in the newspapers that even if potash were obtainable in the Western States, it could not compete with German potash on account of high freight rates. Statements have also been made to the effect that before the Syndicate was formed, an examination was made of possible American potash deposits, and the conclusion was reached that America possessed no deposits large enough to be worked at a profit.

Feldspar and other potash silicates as sources of soluble potash do not appear to be arousing interest in the fertilizer trade or chemical manufacture. The processes which have been proposed—fusion with common salt or with salt and lime, electrolysis, etc.—do not give promise of profitable working. The proposition is a very low-grade one at best. The best potash silicates carry only 12–14% of actual K_2O, and with the addition of fluxes these percentages would be still further reduced. Lixiviation and concentration would probably prove far too expensive, considering the price of the finished product. Soluble potash from insoluble silicates does not appear to be in the realm of the possible at the present time.

The only hope lies in the discovery of soluble sources of supply, and it is for this reason that the fertilizer and chemical manufacturers as well as the general public are awaiting with the greatest interest further announcements from the Department of Agriculture.

W. D. RICHARDSON.

ORIGINAL PAPERS.

THE PREPARATION AND PROPERTIES OF METALLIC CERIUM.*

By ALCAN HIRSCH.

INTRODUCTION.

In view of the amount of research[1] on the rare-earths, it is remarkable that little has been done on the metals themselves. This is easily understood, however, when one considers the scarcity of pure material to work with and the difficulty of reducing these very electropositive elements from their compounds. What metal has been obtained has been, in most cases at least, small in amount and very impure, usually contaminated with the other members of the group. On account of the rarity of the materials to work with, little has been done in a study of the physical and chemical properties of these rare-earth metals, and the field of alloys has been almost untouched.

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* A paper presented at the Twentieth General Meeting of the American Electrochemical Society, Toronto, Canada, September, 1911.

In the present research, cerium, the leading member of the cerium group, was chosen as the rare-earth element to be studied. The investigation was undertaken with a two-fold purpose. First, starting from as pure cerium salt as it was possible to obtain, it was desired to prepare the metal in quantities sufficiently large that its physical and chemical properties could be studied and a large number of alloys could be made. Second, by preparing metal from the unpurified rare-earth residues from monazite sand, obtained as a by-product in the incandescent gas-mantle industry, it was hoped that alloys of commercial value could be obtained. In other words, whereas the application of these residues as oxalates or oxides is very limited to-day, their value might possibly be increased materially if a useful metallic or alloyed product be prepared from them.

The writer gratefully acknowledges his indebtedness to Mr. H. S. Miner, chief chemist of the Welsbach Light Company, for his very generous supply of pure rare-earth salts and rare-earth residues, and to Professors Burgess and Lenher, of the University of Wisconsin, for the facilities of their laboratories and their helpful advice and encouragement during the progress of this research. The electrolytic work was done in the laboratories of Applied Electrochemistry, while the analyses and the chemical preparations were made in the Department of Inorganic Chemistry.

This research was begun in December, 1907, and concluded June, 1911. The actual time devoted to this study covered a period of over three years.

HISTORICAL.

In 1751 Cronstedt[2] discovered the mineral cerite in a mine of Bastnaës. In 1784 Bergmann and d'Elhyar[3] confused the rare-earth with lime, and published an incorrect analysis of this mineral cerite. In 1794 Gadolin[4] discovered the rare-earths in a heavy black mineral, afterwards called gadolinite.

In 1804 cerium was discovered simultaneously by Klaproth[5] in Germany and by Berzelius and Hisinger[6] in Sweden. The first investigator named the oxide ochre earth because of its color, but Berzelius and Hisinger called the new element cerium, after the planet Ceres. About the same time Vauquelin[7] confirmed the discovery of a new earth by analyzing cerite, and then undertook the study of the salts of cerium.[8] In 1814 Berzelius and Galin[9] separated the oxides of cerium and yttrium. Between this period and that of the famous researches of Mosander, numerous articles were published on cerium and the minerals in which it was found, but the material used was necessarily very impure, and what was called at that time cerium oxide was in reality the mixed oxides of the cerium group.

In 1839 Mosander[10-11] announced that cerium oxide was a mixture of two oxides, those of cerium and lanthanum. In 1841 he stated that cerium oxide contained still another oxide, that of didymium. In 1868 Wolf[12] determined the equivalence of cerium and announced that the so-called cerium compounds were mixtures of two or more rare-earth elements. In 1879 Lecoq de Boisbaudran,[13] while examining the didymia obtained from the mineral samarskite, isolated a new element which he called samarium. In 1885 Auer von Welsbach[14] showed that didymia was a mixture of the oxides of two new rare-earth elements, neodymium and praseodymium.

At the present time there are about 15 well identified elements which, for chemical reasons, among other properties that of the insolubility of their oxalates in slightly acid solution, are classified as rare-earths. These rare-earths are usually subdivided into three groups in the order of their basicity—the cerium group, the gadolinium group and the yttrium group. There is no absolute differentiation of one group from another, but rather a gradual transition. Usually only the five elements—cerium, lanthanum, neodymium, praseodymium and samarium—are included in the cerium group.

The present research is concerned with the cerium group, and principally with cerium itself. But in the rare-earths relations between members of the same group are much closer than among other kindred elements, as the platinum metals. For example, the atomic weights of lanthanum, cerium and praseodymium are, respectively, 139, 140.25 and 140.6; therefore the chemistry of one element concerns that of the other members of the group—to a certain degree at least.

Previous Work on the Rare-earth Metals.

Two general methods of preparation have been used for the production of the rare-earth metals:

1. Reduction of the oxide or chloride by one of the very electropositive metals.
2. Electrolysis of a fused salt.

Mosander and Marignac[15] appear to have been the first to produce metallic cerium by a thermal reduction using the alkali metals. Wöhler[16] describes the difficulty of the reduction using sodium metal and cerium chloride, and states that 12 grams of sodium yielded only 50–60 milligrams of cerium metal. Winckler[17] used metallic magnesium and cerium dioxide and obtained a pyrophoric mixture. Recently some attempts have been made to produce the metals by improved methods of thermal reduction. Matignon[18] used metallic aluminum and magnesium, and Schiffer,[19] in Muthmann's laboratory, experimented with the reduction of the oxides by aluminum. From the writer's own experiences in the attempted thermal reduction of these oxides, which is described further on in this article, it appears that the reduction yields either a lower oxide, an impure mixture of partially reduced metal and oxide, or an alloy of the reduced metal and rare metal, such as an aluminum-cerium alloy.

In 1874 Frey[20] published a notice of the preparation of the rare-earth metals in the laboratory of Dr. Schuchardt, in Gorlitz, using the electrolytic method of Bunsen. The following year Hillebrand and Norton[21] published an account of their work on the electrolysis of the fused chlorides of cerium and potassium. They succeeded in producing about six grams of cerium. In 1895 Pettersson[22] attempted to electrolyze the oxides, but produced only the carbides. In 1902 Muthmann[23] and his associates published the first of a very comprehensive series of articles[24] on the metals of the cerium group. Besides preparing the metals of the cerium group, they devised a new type of electrolytic vessel which they found useful in their method of electrolysis. They have also prepared an alloy which they call "mischmetall," which is an alloy of the cerium-yttrium group metals. Borchers and Stockem[25] have devised a method in which they use the double cerium-calcium chlorides, and have patented this process (German Patent 172,529). The above-mentioned electrolytic methods will be referred to again further on in this article.

PREPARATION OF MATERIAL.

The general scheme followed in this research was to use the mixed rare-earth oxides for experimenting on the exact conditions required for the preparation of the desired salt and, after the proper conditions of the process had been determined, to prepare the pure cerium salt. Oxalates of the rare-earths, a by-product of the commercial extraction of thorium and cerium from monazite sand, were employed for these experiments. The oxides, prepared by calcining the oxalates at a temperature of 750–800° C. in a gas muffle furnace, analyzed 97.8 per cent. rare-earth oxides, of which approximately 49 per cent. was cerium dioxide. They dissolved completely in nitric acid, and also in hot concentrated hydrochloric acid on digestion, which is usually taken as a check that the cerium content is less than 50 per cent.[26]

Preparation of Anhydrous Chlorides.

The first salts required were the anhydrous chlorides (composition RCl_3). There are several hydrated chlorides of cerium known, of the compositions: $2CeCl_3.15H_2O$; $CeCl_3.7H_2O$; $CeCl_3.6H_2O$; $CeCl_3.H_2O$. Cerium chloride is similar to magnesium chloride in that when its solution is evaporated to dryness and calcined, HCl is evolved with partial decomposition of the chloride to oxychloride and oxide.

A good many methods have been proposed for the preparation of anhydrous or dehydrated chlorides of cerium, among which may be mentioned the following: Heat the hydrated chlorides with NH_4Cl until the latter salt is completely volatilized.[27] Behringer[28] heated the hydrated chlorides with NH_4Cl in a glass tube in a current of chlorine. Robinson[29] heated the oxalates to a temperature of about 130° in dry HCl gas until all of the oxalic acid had sublimed, then gradually raised the temperature to a red heat. Didier[30] heated CeO_2 in a current of CO_2 and chlorine. Muthmann and Stutzel[31] passed H_2S over anhydrous sulphate heated to a high temperature, and then a mixture of CO_2 and dry hydrochloric acid gas. Mosander[32] burned cerium in chlorine. Moissan[33] attacked the carbide by hydrochloric acid gas at 650° or chlorine at 250°. Meyer[34] converted the oxides to chlorides by vapors of CCl_4.

A number of methods for the preparation of the anhydrous chlorides were tried before a suitable one was found. The large quantity of chloride which was required (several kilograms) necessitated that the preparation should be done in as simple and rapid a manner as was possible. Both aqueous and non-aqueous methods were tried, and below are given the different processes experimented with and their relative advantages and disadvantages.

One of the best methods for the preparation of this type of chlorides (those that decompose on evaporation and calcination from aqueous solution) is to heat the hydrated chloride with NH_4Cl. In the case of cerium chloride, Muthmann[35] describes in some detail this method, and mentions the tediousness and care required. To prepare a kilogram or so may require several days' work to effect the dehydration. The use of a platinum finger crucible is recommended, and not more than 50 grams of the hydrated cerium-ammonium chloride should be heated at a time. The heating must be done very cautiously or the product will be contaminated with oxychloride or oxide. The writer has tested thoroughly this method, and finds it very poor in this case for large scale operations. One set of experiments which was tried will illustrate the difficulties encountered. Two kilograms of the mixed oxides were dissolved in 4 liters HCl (22° Bé.) and about $4^1/_2$ kilograms NH_4Cl were added. Evaporation was carried to dryness in large (35 cm.) porcelain evaporating dishes. About a kilogram of the chlorides was introduced into a large Dixon crucible, which was heated in a gas crucible furnace at a low temperature until the white fumes of NH_4Cl came off copiously. The fumes were conducted out of the window by a suitable flue, and the atmosphere within the furnace was at all times a reducing one. The heating was continued until the contents of the crucible were molten and white fumes ceased to come off. A strong odor of HCl gas and chlorine was noticed toward the end of the operation. The product did not melt to a clear liquid as the properly prepared anhydrous chloride does, but fused to a slimy mass. Analysis showed that the chloride was highly contaminated with oxide, and although 1,100 grams were obtained, the product was unsuitable for electrolysis.

Borchers and Stockem[36] state that many of the difficulties encountered in the dehydration of hydrated cerium chloride can be avoided by the preparation of the double calcium-cerium chloride, and that this salt can be prepared in the anhydrous state without decomposition by simple calcination. These results could not be duplicated by the writer. Forty-seven grams of the hydrated chloride of cerium were dissolved to a clear solution in water slightly acidified with HCl, and 15 grams of $CaCl_2$ were added. The solution was evaporated to dryness and calcined. The salt which was obtained did not melt to a clear solution, and was unsuited for electrolysis.

Dennis and Magee[37] have prepared the hydrated chloride $CeCl_3.7H_2O$, which loses water in a vacuum or over dehydrating agents, whereas the hydrate $2CeCl_3.15H_2O$ does not effloresce when placed over sulphuric acid.[38] It was thought that perhaps the anhydrous chloride could be prepared from the hydrated salt $CeCl_3.7H_2O$. The concentrated solution of the chlorides, prepared by the action of concentrated HCl on the mixed oxides, was cooled to 0° C. by ice, and dry HCl gas was passed into the solution. After a time crystals began to separate out. They were filtered, dried in the air, and the chlorine content determined by titration with standard $AgNO_3$. The per cent. of chlorine was found to be 26.6 per cent., whereas that in $CeCl_3.7H_2O$ is 28.6 per cent. The presence of rare-earths other than cerium probably caused the difference in composition. When this salt was heated in a partial vacuum (water-pump) at 100° for two hours, the loss in weight was 4.4 per cent. When dried over P_2O_5 in a vacuum desiccator for several days, the loss in weight was about 8 per cent. The salt $CeCl_3.7H_2O$ was then dehydrated in dry HCl gas. Small quantities of the salt were placed in several porcelain boats in a porcelain tube furnace through which dry HCl gas was passed. The maximum temperature in the tube was 210°, and the average temperature was 195°. The product in the boat placed in the center of the tube lost 35 per cent. in weight, and analysis showed a chlorine content of 39.3 per cent. The chlorine content of the anhydrous chloride $CeCl_3$ is 43.2 per cent. The chloride so prepared melts to a clear liquid. Attempts were then made to prepare the anhydrous chloride on a larger scale by this method: 1,500 grams of the mixed oxides were converted into chlorides, and then the hydrate $CeCl_3.7H_2O$ was prepared by the method of Dennis and Magee, described above. The yield of salt was very small, and the operation is a difficult one to perform on a large scale, due to the fact that a low temperature is necessary and the absorption of HCl gas in water is accompanied by a considerable evolution of heat. Moreover, a simple method was found for preparing the monohydrate, and as the dehydration of the septa-hydrate passes through the stage of the monohydrate, this method was abandoned.

As the dehydration of the chlorides appear to be the principal difficulty in the preparation of the anhydrous chlorides, it was thought that a suitable process might be developed by the use of non-aqueous solvents. As the action of non-aqueous solvents was found to be somewhat slower than the action of aqueous ones on cerium compounds, it was desirable that a readily decomposable substance be used as the starting material, and the rare-earth carbides were chosen for this reason.

The carbide* RC_2 was prepared by heating the mixed oxides with powdered graphite in an arc furnace. Several kilograms of this material were prepared according to the method of Moissan.[39] The proper mixture to be heated was found to be 500 parts mixed oxides and 132 parts finest graphite powder. When a graphite crucible was used as one terminal and a graphite rod (about 1 inch diameter) as the other, the carbide was easily prepared on a large scale by using a 25 kw. arc (AC or DC). Care should be taken to protect the eyes properly as the rays emitted from the hot mass are especially harmful as they contain a certain amount of ultra-violet rays.

Alcoholic HCl,† made by passing dry HCl gas into cooled absolute alcohol, acts readily on the carbides. The solution of the chlorides prepared by this method always contains more or less graphite, and is very difficult to filter because of its viscosity. By evaporation to dryness, the anhydrous chlorides are obtained, but care must be taken to prevent absorption of moisture, as the syrupy liquid is extremely hygroscopic. Several minor difficulties are encountered in this method, the principal ones being the solubility of acetylene in absolute alcohol (6 times as soluble as in water) and the lesser solubility of the chlorides in absolute alcohol (one-third as soluble as in water). Because of the above disadvantages, and the expense involved in the use of absolute alcohol and its subsequent loss on evaporation, this method was not suitable to large scale operations. The action of HCl gas and chlorine on the carbides gives chlorides which are highly contaminated with carbon and are therefore useless for electrolytic purposes, as carbon in a finely divided state with the chlorides will form carbides on electrolysis.

In view of the fact that the non-aqueous methods were not suitable for the problem at hand, resort was again made to dehydration methods. It was found that by treating the mixed oxides with concentrated HCl, evaporating to dryness, adding more HCl and repeating the process a number of times, a product was obtained corresponding to one of the lower hydrates of the chlorides. This white solid was very hygroscopic, and dissolved in water with avidity and evolution of considerable heat; when broken into lumps and calcined at a low temperature (not exceeding 125°) on an asbestos-covered hot plate further dehydration occurs without decomposition. The heating should be continued for a long time (about 12 hours), and the temperature must be kept low. If these directions are followed, a product corresponding approximately to the monohydrate is obtained. The great difficulty is to get rid of the last molecule of water, which is the most tightly bound of all, without decomposing the chlorides.

Matignon[40] and Bourion [41] have done a great deal of work on the preparation of anhydrous chlorides. They have found that certain chlorides of the metalloids, especially those of phosphorus and sulphur, act as catalyzers in the dehydration of hydrated

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* Moissan (*C. R.*, **124**, 1233) states that pure CeO_2 (free from iron and other earths) may be prepared from cerium carbide by fractional treatment of the carbides with dilute HNO_3. A modification of this method for the preparation of cerium dioxide free from the other rare-earths was made as follows: 100 grams of the mixed rare-earth carbides were ground to a fine powder and were treated with a small amount of dilute HNO_3. After the second treatment iron could not be detected in the residue by the sulphocyanide test. A larger amount of dilute HNO_3 was added and the solution after filtration was treated by Mosander's method. (Chlorine passed into the solution which had been made alkaline with KOH.) The precipitate after washing showed only a very faint absorption spectrum. For rapid preparation of cerium dioxide this method appears to be very good. The oxide prepared by this means is yellow when calcined at 100°, but turns darker when heated to 1000°.

† Meyer and Kess (*Ber.*, **35**, 2622) have used alcoholic HCl for the preparation of cerium salts. They found that this solvent has no action on the oxides but reacts readily with the carbonates. They did not use the carbide.

chlorides, and that in the presence of dry HCl gas, chlorine and sulphur monochlorides (S_2Cl_2) the chlorides of silicon, aluminum, thorium, neodymium, praseodymium, samarium and vanadium can be prepared in the anhydrous condition.

For the problem at hand this method had apparently many advantages and few disadvantages, chief of which was the very disagreeable nature of sulphur monochloride. It was resolved, therefore, to try out this method on the preparation of the anhydrous mixed chlorides. About 400 grams of the hydrated chlorides were placed in a porcelain tube furnace through which was passed a mixture of chlorine, S_2Cl_2, and HCl gases. The maximum temperature was about 300°, and the heating was continued for two and one-half hours. The product in the center of the tube was fritted together, and a sample for analysis was taken from this portion; 1.4 per cent. was insoluble, and the chlorine content of the soluble part was 42.4 per cent.—the per cent. of chlorine in $CeCl_3$ is 43.2 per cent. The product melted satisfactorily, and the method seemed suitable, so that a plan was devised for its application on a larger scale.

A terra-cotta drain pipe, four inches (10 cm.) in diameter and four feet (1.2 m.) in length, was fitted at both ends with graphite caps, through which passed short pieces of glass tubing, two at one end and one at the other. The furnace was a circular-flame tube furnace in which the pipe could be heated gradually and uniformly, and the temperature was under positive control. The monohydrated chlorides, prepared by the method previously described, were dehydrated, about a kilogram at a time. The salt was spread evenly in the pipe, in a layer about $^3/_4$ inch (2 cm.) thick. The caps were then inserted and the ends heavily luted with a mixture of magnesia, asbestos fiber, cement, fire-clay and water, and allowed to dry, when a joint practically gas-tight was obtained. Dry HCl gas was passed over the chlorides and as soon as the air was displaced the heating was commenced with a small smoky flame. After the tube was warm, chlorine and S_2Cl_2 vapors, as well as dry HCl, were passed through the tube and the temperature was gradually raised to just below 400°. The dehydration is completed in about three hours if the temperature is correctly adjusted, but may take longer. The anhydrous chlorides are placed, while still warm, in dry bottles, and the corks paraffined in. Care must be taken to prevent the sewer-pipe from cracking when being heated, and this tendency forms one of the principal weaknesses of the process. A metallic container can not be used in the dehydration on account of the highly corrosive action of the vapors.

The sulphur monochloride seems to catalyze the dehydration process, and has the further function, together with the chlorine gas, of reconverting to chloride any oxide or oxychloride which may form. If the temperature is too high, oxide or oxychloride may form even in the presence of chlorine and sulphur monochloride. The dehydration may be carried out by HCl gas alone, and a scheme was devised for preparing pure anhydrous cerium chloride using this method. Since the process was the outcome of much work and of experience in the handling of the chlorides, it is described here in some detail.

The double cerium ammonium nitrate from the fractionating vats, where it has been purified and separated from the other rare-earths by fractional crystallization, was used. The absorption spectrum of a concentrated solution of the nitrates showed only the faintest traces of the neodymium and praseodymium bands. The contents of a large bottle containing five kilograms of the double nitrates was divided into four portions and placed in fourteen-inch (35 cm.) porcelain evaporating dishes. The dishes were filled with concentrated HCl and placed on steam-heated sand-baths. Each dish was suitably protected from drippings from the hood by wooden covers raised a few inches above the tops of the dishes and supported on silica bricks. Fresh acid was added daily as required and the evaporation continued for about three weeks, at the end of which time the nitrates had been completely converted to chlorides and all the ammonium salts had been expelled. The white solid was broken into lumps and heated on an asbestos-covered hot plate to convert it to the monohydrated chloride. The final dehydration was carried out as follows (see Fig. 1): About 400–500 grams were placed in a ten-inch porcelain evaporating dish. A short-stem funnel about nine inches in diameter was inverted and placed over the salt. A layer of asbestos fiber was packed tightly around the outside edge of the funnel and plaster of Paris set over this. A glass tube passing through the stem of the funnel and reaching to just above the layer of chloride conducted in the dry HCl gas, which was passed at a rapid rate over the heated chloride. The salt was stirred around from time to time by means of a long, thick glass rod. The heating was done gradually and the progress of the dehydration could be watched, through the glass funnel, and its completion checked nicely. The anhydrous chloride was placed, while still warm, in dry glass vessels, and the corks paraffined in to exclude moisture from the extremely hygroscopic product.

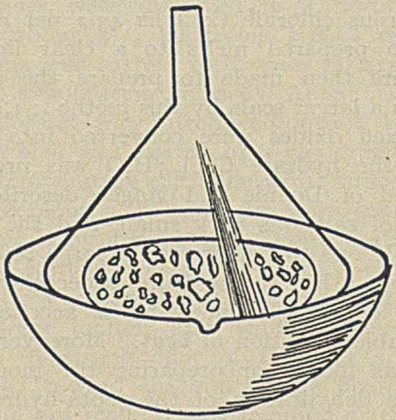

Fig. 1.

The chloride prepared by this method melts to a clear, limpid liquid, and is suitable for electrolysis.

The process meets practically all the requirements—it gives a suitable product, it is rapid, inexpensive and simple, the progress and completion of the dehydration can be watched, overheating may be avoided, and large amounts of chloride prepared in the minimum amount of time. Chlorine and sulphur monochloride may be used in addition to the dry HCl gas, but this was not found necessary, as the water was driven off rapidly and completely without their presence.

It was observed that the anhydrous rare-earth chlorides may be partially converted into oxides or oxychlorides if they were carelessly heated in the presence of air. For this reason experiments were conducted on melting the chlorides in a non-oxidizing atmosphere in a Rose crucible. In the presence of carbon dioxide some oxychloride was formed, and in an atmosphere of carbon monoxide a crust of brownish oxide appeared.

The best method of melting the anhydrous chlorides without decomposition was found to be by heating a small portion in a covered crucible until a clear melt was obtained, and then introducing successive small portions of the chlorides to the melted portion. In this manner circulation of air is avoided, as the crucible is kept covered. A good way is to first melt sodium or potassium chlorides, or a mixture of these, and then to add small amounts of the rare-earth chlorides, keeping the crucible covered as much as possible. A small amount of oxide or oxychloride will "gum up" the entire melt, and for electrolysis this condition must be carefully guarded against.

Preparation of Anhydrous Fluorides.

Another salt required in large amounts was the anhydrous mixed fluorides, RF_3. This preparation involves some of the difficulties encountered in the preparation of the anhydrous chlorides. The fluorides are more stable and less hygroscopic than the chlorides, but they are more corrosive in their action on apparatus. Porcelain vessels can not be used, and one is almost entirely limited to lead vessels in the preparation of these fluorides. However, lead linings are easily placed in evaporating dishes, especially in the large enameled iron ones, and five-gallon jars made of lead containing 10 per cent. antimony were found very convenient in this work.

A few methods are found in the literature for the preparation of anhydrous cerium fluoride, CeF_3, but not many. The fluorides of cerium, especially the hydrated ones, are insoluble in water and are gelatinous precipitates usually obtained by double decomposition.

The tetrafluoride $CeF_4.H_2O$ is found in nature as fluocerite, and when this mineral is heated it decomposes, forming the impure anhydrous fluoride CeF_3.[42] By precipitating cerous nitrate with hydrofluoric acid Jolin[43] obtained a gelatinous precipitate, which after drying over sulphuric acid corresponded to the formula $2CeF_3.H_2O$. When this substance was heated it decomposed, leaving a residue of oxide.

In the preparation of the anhydrous rare-earth fluorides both dry and wet methods were tried. Hydrofluoric acid gas was passed over a small amount of the pulverized carbides placed in an iron tube and heated to a temperature of about 200°. The hydrofluoric acid gas was prepared by heating CaF_2 with concentrated H_2SO_4 in a copper retort. Some fluoride was formed, but was contaminated with carbon and undecomposed carbide, and the method was regarded as unsuccessful.

The action of concentrated HF on the oxides was tried. A small amount of the mixed oxides was heated in a platinum dish with successive portions of concentrated HF. The action was vigorous at first, but soon stopped, and the residue was a mixture of oxide and fluoride.

As the anhydrous fluorides were required, a process in which no water was used obviated the subsequent removal of that water, and seemed to be at least worthy of trial. The chlorides were boiled with absolute alcohol until a concentration solution was obtained, which was transferred to a lead tub placed in hot brine, so that the precipitation might be done from a hot solution, and HF gas passed into the hot chlorides. The objections to this method are that the fluorides so prepared are contaminated with some chloride. Furthermore, the saturation of the hot alcohol with HF gas is a very slow process, and the fluorides are extremely difficult to filter on account of their gelatinous nature. If the precipitation is done in the cold, the fluorides come down in a slimy condition almost impossible to handle, hence the reason for precipitating from hot solution. While the precipitation may be done by the action of a concentrated solution of hydrofluoric acid on the aqueous solution of the chlorides, the fluorides settle far less readily in water than in alcohol. Consequently, on account of the above reasons, the next modification in the process was to dissolve the mixed oxides in concentrated HCl, concentrate the solution and add the requisite amount of concentrated HF to the hot solution. After allowing the precipitate to settle, the supernatant liquid was siphoned off, alcohol added, the whole stirred thoroughly, the precipitate allowed to settle, the liquid siphoned off and the treatment with successive portions of alcohol repeated several times. The fluorides were dried at a low temperature, and were pink in color. They melted at a fairly high temperature (about 900–1000°) to a clear liquid, and the process was satisfactory except for the time required for the precipitates to settle.

In order to flocculate the fluorides so that they could be more easily filtered, the precipitate of the fluorides was placed in a round-bottom Jena flask about half full of absolute alcohol, and heated in an autoclave at a temperature of 130° and a pressure of 90 pounds per square inch. The product so treated seemed to settle somewhat more rapidly, but filtered very slowly indeed.

After many trials, the most satisfactory preparation of the anhydrous fluorides was found to be best effected by the following method: About a kilogram of the mixed oxides was placed in a large porcelain evaporating dish and digested in a steam closet with concentrated HCl until a clear concentrated solution of the chlorides was obtained. The hot solution, containing only a slight excess of hydrochloric acid, was transferred to a five-gallon lead jar and concentrated HF added to complete precipitation. The fluorides were allowed to settle somewhat, as much of liquid siphoned off as was possible, and washed twice with hot water and several times with 95 per cent. alcohol. Only a few minutes' time was allowed after each washing for the precipitate to settle. The fluorides were then placed in a lead-lined cage-centrifuge, and most of the remaining alcohol removed in this manner. Absolute alcohol was added and the solution evaporated to dryness without decanting. The absolute alcohol dehydrates the centrifuged fluorides very well. They were then dried at 100°, and the temperature raised to 200° at the end. About six kilograms of the fluorides were prepared in this manner. The process is a fairly satisfactory one, and as no filtering is done, the method is fairly rapid.

PREPARATION OF METALLIC CERIUM AND MISCHMETALL.

Thermal Reductions.

Thermal reductions were tried in the hope of producing rare-earth metals by this simple means. Previous work of this nature has already been referred to.[15–19] Magnesium and calcium shavings and aluminum powder were used as reducing agents on the mixed oxides. These experiments were conducted in electrically-baked magnesia linings placed in graphite containers. Carbon and silicon were also used to reduce the oxides, but external heat was applied to give the high temperature required. No metal was formed in these last instances but the carbides and silicides respectively. The carbide RC_2 is pyrophoric, but the silicide RSi_2 is not. Reductions using magnesium and calcium in excess gave alloys, many of which were pyrophoric.

Several trials to reduce the oxides with aluminum are here recorded:

$$3R_3O_5 + 10Al = 5Al_2O_3 + 9R$$

150 grams mixed oxides require 27 grams aluminum.

$$3BaO_2 + 2Al = Al_2O_3 + 3BaO$$

507 grams barium peroxide require 54 grams aluminum.

The following charge was weighed out, intimately mixed and fired by means of magnesium wire and thermit igniter.

	Grams.
Mixed oxides	150
Aluminum powder	40
Barium peroxide	120

The reaction was vigorous, but not violent. A five-gram lump of metal and many small globules were obtained. The specific gravity of the metal was greater than that of aluminum.

In another experiment the following charge was used:

	Grams.
Mixed oxides	200
Aluminum powder	61
Barium peroxide	200
Black thermit mixture	50

The black thermit was used to produce a higher temperature and also for the reason that the affinity of cerium for iron was thought to be greater than that of cerium for aluminum; 35 grams of hard-brittle alloy were obtained, but the content of rare-earth metals was low.

In the case of these thermal reductions, either an alloy, a compound or a lower oxide of the rare-earths was obtained. Owing to the high heat of formation of these oxides, the failure of alumino-thermics in the production of metal was only to be expected. The writer believes that a study of the equilibrium conditions of these reactions would form an interesting and valuable research and might result in the discovery of lower rare-earth oxides.

Earlier Work on the Electrolysis of the Anhydrous Chlorides.

The previous work on the electrolytic preparation of cerium has already been referred to. The method of Bunsen, which the earlier investigators used, is described as follows:[44] "In a porcelain crucible, in which the mixed chlorides of sodium and potassium has been melted, small amounts of anhydrous cerium chloride were introduced by means of a small porcelain spatula. An annular piece of iron was used as anode, and the cathode consisted of a platinum wire, protected by a short piece of clay pipe stem. The temperature of the fused bath was lowered until a thin crust formed on the surface of the bath, when the electrolysis was commenced. Globules of cerium rose to the surface and burned with explosive force. Hillebrand and Norton thus obtained metallic globules to the amount of six grams."

At one time the writer tried to duplicate the above experiment, but was unable to collect any metal. The platinum cathode was badly attacked; in fact, part of it melted off, due to formation of an alloy with cerium.

For a survey of Muthmann's work on the rare-earth metals the reader is referred to the original reference.[23–24] The type of vessel used in the electrolysis of the chloride is shown in Fig. 2, and is now generally known as the Muthmann cell. It is a semi-water-jacketed vessel, constructed of copper, and may be used with or without the heating circuit. The principal objection which the writer has to the cell is its complicated nature. The cathode should be insulated carefully, and this is difficult, as the asbestos packing is attacked by cerium metal, and during the course of the electrolysis the insulation is apt to be destroyed and the walls of the vessel may act as cathode, with the subsequent contamination of cerium with copper. This is especially liable to occur if the temperature of the bath is too high. The heating circuit must also be insulated from the walls, and the carbon heating rods are liable to crack and break. Unless the contents of the cell are poured or tapped at the completion of the electrolysis, the entire cell has to be dismantled after each run. When worked on a small scale, the manipulation of this electrolytic cell is a troublesome and difficult operation.

In the present research, numerous runs were made before more than traces of metal were obtained. It is believed by the writer that an account of failures is often fully as important as that of successes, as it is only by correction of faults that successful results are obtained. Therefore a brief account of the earlier unsuccessful attempts to produce rare-earth metal are here given. It was only by a complete understanding of the reasons for failure that a successful solution of the problem was accomplished.

The different types of cells used where anhydrous mixed chlorides were employed as the electrolyte are shown in Figs. 3 to 5.* They were all constructed of the same material, graphite. The anodes were of graphite, but in the case of the insulated cathodes these were sometimes of graphite and sometimes of iron. In many cases where a graphite crucible was used as both containing vessel and cathode, the melting was done in a resister furnace, and then the electrolysis was begun. In some instances the heating was done by alternating current, and could be maintained and regulated during the course of the electrolysis. The melting of the electrolyte was sometimes done by a small thin carbon heating rod placed between electrodes, as shown in Fig. 2. An arc could not be used to melt the chlorides, as they are decomposed at that temperature.

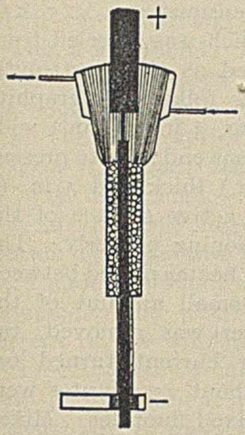

Fig. 2.

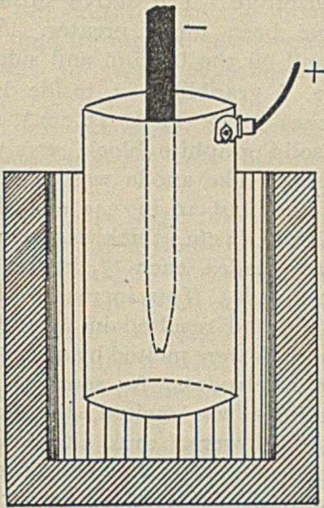

Fig. 3.

The principal difficulties encountered in these experiments were the following:

1. The salt would not melt to a clear liquid.

2. The electrolyte would remain liquid for a time, but would eventually solidify.

3. The IR drop across the cell and the amperage would vary.

4. The anode would not functionate properly.

5. On completion of the electrolysis, no regulus of metal was obtained.

6. Minor difficulties, such as short-circuiting of insulated cathodes, leakages, fracture of electrodes, etc., liable to happen in any fused electrolysis, were encountered.

The reasons for the above difficulties were found by experience to be explained as follows:

1. If the chlorides did not melt to a clear liquid, then either the chlorides were not anhydrous or they were decomposed in the process of fusion. The proper manner of melting the chlorides has already been discussed in sufficient detail.

2. The "gumming-up" was caused either by the formation of a higher melting salt, as the oxide or carbide, or the temperature of the bath was too low (see 4, below).

3. As the generator voltage and the external resistance were constant, changes in the voltage across the cell and the amperage were caused by a variation of the internal resistance of the cell. This variation was caused by the following factors: Change in temperature of the bath; depletion in the electrolyte, or segregation, such as double layers, etc.; formation of intermediate products of varying resistance, such as sub-chlorides; differences in thermal conductivity of the electrolyte at different stages of the electrolysis; etc. It was found that the potential difference and the amperage of any one cell can vary only between certain limits for successful electrolysis. The heating value of the current (C_2R) in cases where no external heat is applied must be such as to keep the temperature of the bath at a certain value. If the temperature of the electrolyte is too high it is impossible to successfully electrolyze in the case of cerium chloride.

4. The function of the anode was (1) to cause the separation of chlorine and (2) to supply most of the heat necessary to keep the bath fused.

(1) In all these experiments the amperage was such that, if the cell was working properly, there was a copious evolution of chlorine gas. In many cases the voltage across the bath and the amperage would be approximately the proper values, and yet very little chlorine would be evolved. This may occur under several very different conditions. If the temperature of the bath is low, the semi-fused chloride is a very good conductor, and the entire bath may behave as a conductor of the first class. In this case practically no chlorine will be evolved. Again, if the temperature of the bath is too high, little chlorine is given off. This is due to the fact

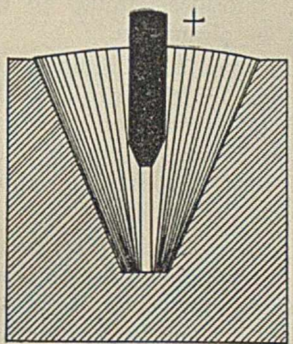

Fig. 4.

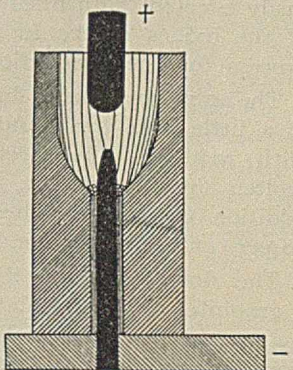

Fig. 5.

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* The crucible shown in Fig. 4 was split longitudinally into two sections, which were cemented together by graphite-molasses paste and clamped firmly together. This makes a very convenient form of electrolytic cell, as it can be easily dismantled, and also very quickly reassembled.

that at the cathode the chloride is partially reduced to subchloride, which diffuses to the anode and is there oxidized by the chlorine to chloride. There is a narrow limit of temperature where true electrolysis occurs, that is, where anhydrous $CeCl_3$ is decomposed by the current to metal and chlorine.

(2) In cases where the containing vessel acted as the cathode, anodic current density was much greater than the cathodic, consequently most of the heat was supplied to the cell by the anode. In the preliminary experiments the anodes were of graphite, but with the same diameter anode and the same current the heating is greater with a carbon than with a graphite anode. In some of the later runs carbon was used as the anode material for the reasons mentioned above. If the diameter of the anode is too great, a large current is required to keep the bath molten. Besides, the anode is brought nearer the walls and most of the current may pass through the upper part of the cell. This should be avoided, as the path of least resistance for the current should be from the anode to the bottom of the cell, as this insures good circulation of the electrolyte and the deposition of the metal in a united form. If metal is deposited on the upper walls, some is apt to become oxidized by contact with the air, and this may result in the bath becoming viscous.

5. Many of the reasons for failure to obtain a regulus of metal have been given above. The metal may be deposited in a finely-divided, unfused condition, and may be disseminated throughout the body of the electrolyte. It may be totally or partially soluble in the electrolyte (for instance, Li in LiCl), or the metal may react with the products at the anode (as chlorine) or the material of the cell (with copper forming an alloy, or with graphite forming a carbide).

Electrolysis of the Anhydrous Fluorides.

When it was found that the electrolysis of the chlorides was such a difficult process, it was thought that the electrolysis of some other salt might be more easily effected. Muthmann [24(c)] has used the solution of the oxides in the fused fluorides, similar to the process for the production of aluminum.

The anhydrous mixed fluorides melt at a temperature of a little over 900°, and dissolve the mixed oxides with avidity. The electrical conductivity of the molten fluorides is low, but increases rapidly with addition of oxides. The solution containing about 20 per cent. of oxides conducts very well.

The first cell tried with the fluorides contained a graphite cathode insulated from the graphite vessel by a porcelain ring. During the electrolysis the porcelain was badly attacked by the fused fluorides. Even a Dixon crucible was badly eroded, as the fluorides attacked the silicate binder. It was found that graphite was one of the few substances that would withstand the high temperature and the action of the fused fluorides. A vessel made of graphite plates, luted on the edge with graphite-molasses paste, clamped together with iron bands and previously baked, leaked during the electrolysis. Although the vessel was embedded in magnesia flour to prevent oxidation, the high temperature of the bath (well over 1000°) caused the luting to break down.

A summary of the results of the runs using fluoride-oxide electrolyte are here given.

1. 2,500 grams anhydrous mixed fluorides were melted in a resister furnace. The fused fluorides readily dissolved 450 grams of mixed oxides. The molten bath was electrolyzed, using 450 amperes at a pressure of 14 volts. 10–15 grams of impure metal were obtained. The electrolysis was unsatisfactory, as the anode was not properly "wet" by the electrolyte. The active surface of the anode should have been much greater. A layer of carbide was found on the bottom and sides of the crucible.

2. A graphite box, inside dimensions $4\frac{1}{2} \times 5 \times 6$ inches ($11 \times 12 \times 15$ cm.), which was chiseled from a solid graphite block, was used as the electrolytic vessel. The anode was made as follows: A graphite block about 16 in. (40 cm.) long, 3 in. (8 cm.) wide and 2 in. (5 cm.) thick was cut at one end so as to present three blades, each $\frac{1}{2}$ in. (1 cm.) thick and 3 in. (8 cm.) wide. This increased the active surface of the anode and resulted in its functioning properly. The fluorides were melted by a carbon heater placed between the electrodes. As soon as a small amount of the fluorides was melted, the heater was removed, the anode lowered and alternating current turned on. 1,000 amperes at 24 volts for about 25 minutes were required to melt 4,300 grams mixed fluorides. Mixed oxides were added gradually and then direct current switched on. 650–750 amperes at a pressure of 10 volts were used. Oxide was added gradually during the course of the run, which was continued for about an hour, at the end of which time the solution solidified. 4,300 grams fluoride and 1,600 grams oxide were used in all. Small amounts of metal were scattered throughout the mass, but no regulus was obtained. At the bottom of the vessel was found a black layer of carbide. The melting point of the fluoride-oxide mixture was about 1400°.

The principal difficulties encountered in the electrolysis of the oxides dissolved in the fused fluorides were:

1. Oxides must be added to the fluoride to make a sufficiently conductive solution, and the melting-point of the bath is very high.

2. At the high temperature of the bath, rare-earth metal and graphite combine to form carbide.

Attempts were made to electrolyze a solution of the oxides dissolved in a mixture of fused potassium fluoride and rare-earth fluorides. Violent explosions ejected a large portion of the electrolyte during the run, due perhaps to the deposition of alkali metal, which was immediately vaporized at the temperature of the bath.

One of the principal difficulties in all the previous electrolyses had been the formation of carbides, which made the bath viscous and unfit for electrolysis. It was thought that if a non-carbon cell was used, the formation of carbide would be less likely to occur, as the only carbon in the cell would be the anode. On account of their corrosive action and high melting point the fluorides could not well be used in other than carbon vessels. It was therefore decided to try the electrolysis of the mixed chlorides in a wrought-iron vessel.*

Later Work on the Electrolysis of the Anhydrous Chlorides.

1. The electrolytic vessel was a thin-walled wrought-iron crucible about 3 in. (8 cm.) high and 2 in. (5 cm.) average diameter. The anhydrous mixed chlorides were fused by means of a thin carbon rod, heated electrically to incandescence, and electrolyzed with a current of about 50 amperes for several hours. The electrolyte remained fluid during the entire course of the electrolysis. About 30 grams of semi-fused metal were obtained.

The iron crucible was not attacked. The success of this run led to experiments on the best conditions for electrolysis on a larger scale.

2. The electrolytic vessel was a large iron crucible $5^{1}/_{2}$ in. (14 cm.) maximum inside diameter and 7 in. (18 cm.) high. The anode was a carbon rod $1^{1}/_{2}$ in. (4 cm.) in diameter. A small amount of sodium chloride was fused, and the mixed chlorides were added in small amounts until a fused bath was obtained. The electrolysis was maintained with a current of 130 amperes for four hours at a pressure of 12–18 volts. Small amounts of anhydrous potassium fluoride (about 10 grams at a time) were added occasionally to dissolve what little oxide was formed and so keep the bath perfectly fluid. The amount of additional salts used (KF plus NaCl) in all was about 10 per cent. by weight of the rare-earth chlorides. A lump of partially fused metal was obtained, which when re-melted under NaCl weighed 120 grams. The number of ampere hours used was 520, and the ampere efficiency was $13^{1}/_{2}$ per cent. The crucible was not attacked.

3. The object of this run was to try the value of an insulated cathode. Previous experience had taught that if the insulated cathode was iron and a fairly large current used (about 200 amperes) the iron cathode would become so hot that an alloy would be produced. Consequently iron was not used as the cathode in this electrolysis. The electrolytic vessel consisted of a 6-in. (15 cm.) length of a 3-in. (8 cm.) iron pipe screwed into a reducing-cap carrying a short piece of 2-in. (5 cm.) pipe. The cathode consisted of a long rod $1^{1}/_{2}$-in. (4 cm.) graphite insulated from the sides of the 2-in. (5 cm.) pipe by asbestos fiber and encased at the bottom in plaster of Paris. A sketch of this cell is shown in Fig. 6. The anode was a graphite rod $1^{1}/_{2}$ in. (4 cm.) in diameter. A current varying from 180 to 200 amperes at a pressure of 20 volts was used for nearly four hours. A regulus of metal weighing 135 grams was found at the bottom of the vessel. Below the metal was a black layer of carbide. The number of ampere hours was 712, and the ampere efficiency was 11 per cent. The electrolyte consisted of the mixed chlorides, to which were added, during the course of the run, small amounts of anhydrous potassium fluoride, sodium chloride and barium chloride. The object of the last-named salt was to increase the resistance of the bath so that the electrolyte was kept well fused and metallic conduction of the bath prevented. It must be remembered that where a graphite anode was used, a higher voltage was required to keep the bath fused.

The results of the above three experiments showed: (1) That rare-earth metal could be produced by electrolysis of the chlorides in iron vessels; (2) that the use of an insulated cathode of graphite gave a lower current efficiency and resulted in some of the metal being converted to carbide; (3) that it was necessary to regulate the temperature of the bath so as to have the electrolyte well fused and yet well below the alloying temperature of iron and rare-earth metal; and (4) that control of the electrolysis could be maintained by judicious addition of small amounts of potassium fluoride, sodium chloride and barium chloride.

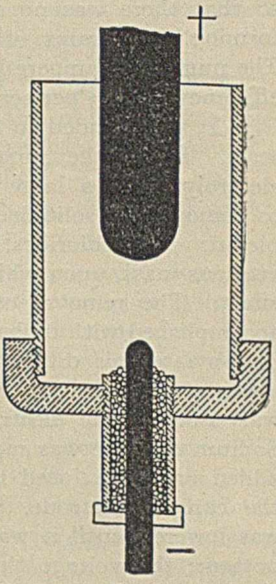

Fig. 6.

The above experiments in which the anhydrous mixed chlorides were used were so successful that the method of electrolysis was applied to pure anhydrous cerous chloride, and the runs are here described.

1. The electrolytic vessel was a thin-walled wrought-iron crucible, maximum diameter about 4 inches. The anode was a round graphite electrode 1 inch in diameter, and the iron crucible was made the cathode. A small amount of sodium-potassium chloride was first melted, and then cerous chloride added. During the course of the electrolysis, rather large amounts of the alkali chlorides were used. A current of 110 amperes was employed for two hours, at the end of which time the electrolyte solidified. Forty grams of fairly-well-fused metal was obtained. The number of ampere hours was 220, and the ampere efficiency was 11 per cent. Too much alkali chlorides was added during the electrolysis, and this fact, together with the high temperature of the bath,* accounts for the efficiency.

2. A crucible similar to the one described in the above experiment was used both as the containing vessel and cathode. A corrugated graphite anode $^{5}/_{8}$ in. (1.6 cm.) in diameter was used. 250–300 grams of anhydrous cerium chloride and about 10 per cent. sodium chloride were used. The electrolysis

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* Kindly suggested by Dr. W. H. Walker, of the Mass. Inst. Tech.

* In many electrolyses a high ampere efficiency is obtained only if the bath is kept near its melting point. As the temperature is raised the efficiency decreases. This is especially true in the case of fused lead chloride and fused caustic soda, where if the temperature of the bath is high, no metal at all is obtained. See these Transactions, **19**, 167–168 (1911) (Discussion).

was continued for 1½ hours, using 75 amperes at 15 volts. The bath was kept near its melting-point, so that there was no danger of a cerium-iron alloy forming. 65 grams of cerium metal were obtained. The number of ampere-hours was 112, and the ampere efficiency was 33 per cent.

3. It was decided to try the electrolysis on a larger scale. When the mixed rare-earth chlorides were electrolyzed in a large iron crucible, it was difficult to remove the solidified salt after the run was completed. The chlorides, after cooling, form a hard, vitreous mass, upon which even a cold-chisel has little effect. The removal of slag and metal was always accomplished with difficulty and loss of some material. To obviate this difficulty a 7-in. (18 cm.) length of a 3-in. (8 cm.) iron pipe, screwed into a cap for a bottom, was used as the electrolyzing vessel (see Fig. 7). Sodium chloride was melted first, and cerous chloride added until the fused mixture conducted well, when the carbon electrode, 1¼ in. (3 cm.) in diameter, was lowered until it was within an inch or so of the bottom; the voltage then sank to the proper value, 12 volts, and electrolysis began. The volume of the bath, of course, constantly decreases during the electrolysis, and fresh cerous chloride must be added from time to time. About every forty minutes the anode was raised until it just dipped below the surface of the bath. This increased the voltage across the bath and caused a rapid heating of the electrolyte. After a few minutes the anode was lowered until the voltage was properly adjusted, when electrolysis recommenced. The voltage varied from 12 to 14 volts, and the average current used was 200 amperes, for four hours. The electrolyte became slightly viscous toward the end of the run, but the electrolysis proceeded satisfactorily, as was indicated by the appearance of the bath, the voltage across the cell and the evolution of chlorine. Over a kilogram of cerous chloride was used. A well fused ingot of metal weighing 580 grams was obtained. The number of ampere hours was 800, and the ampere efficiency was 41½ per cent. The cap could not be removed at the completion of the electrolysis, but the crucible was unattacked by the cerium. The small amount of iron introduced was caused by oxidation of the heated vessel near the top, the solution of this iron oxide in the electrolyte and its immediate reduction to metal when in contact with cerium.

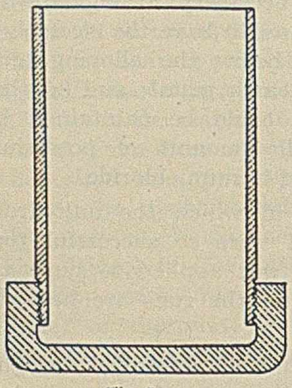
Fig. 7.

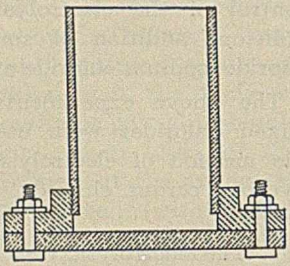
Fig. 8.

4. In order to facilitate the removal of electrolyte and metal at the end of a run, the following vessel was devised: It consisted of a 3-in. (8 cm.) iron pipe screwed tightly into a 5-in. (13 cm.) iron flange, to which a bottom plate was attached by means of four large bolts and nuts (see Fig. 8). The electrolyte was cerous chloride containing a small percentage of sodium chloride, to which very small amounts of potassium fluoride and potassium fluoride-barium chloride mixture were added when required (about every half hour or so). The function of these additional salts has already been explained in detail. The voltage was kept at its proper value, which should not be greater than 15 volts. The average current used was 200 amperes, for three hours. The electrolysis required attention about every twenty minutes; that is, the anode needed slight adjusting or the temperature had to be corrected. An ingot weighing 380 grams was obtained. The number of ampere hours was 600, and the ampere efficiency 36.5 per cent.

The electrolyte remained liquid during the entire course of the electrolysis. About 1½ kilograms of cerous chloride were used. The cell held perfectly, and at the end of the run the electrolyte and metal were easily removed. This type of electrolytic vessel is highly recommended for similar work. Care should be taken that the flange and bottom plate are well faced and that the lap is wide enough (at least 1½ in. (4 cm.)).

ANALYSIS OF CERIUM AND "MISCHMETALL."

Two methods of analysis were used in this research for the determination of cerium:

1. *Gravimetric.*—The cerium group was separated from all the other metals by precipitation of the oxalates in faintly acid chloride or nitrate solution, by means of boiling oxalic acid. Calcination of the oxalates at blast lamp temperature gave the oxides (in the case of cerium the dioxide CeO_2) which were weighed.

2. *Volumetric.*—A modification of Browning's[45] method was used. It depends upon the oxidation of cerous salt to ceric, in alkaline solution, by means of potassium ferricyanide. Browning determined the excess of ferricyanide.

The modification was as follows: A slight excess of a dilute solution of potassium ferricyanide was added to the solution of cerous salt, and KOH added. This precipitation was usually done in a bottle, which was afterwards centrifuged. The supernatant liquid was decanted through a small Gooch filter to guard against any loss of precipitate. The ceric hydroxide was washed two or three times with hot concentrated KOH to remove the ferro- and ferricyanides centrifuging after each washing. The ceric hydroxide was then treated with potassium iodide solution, whereby the cerium is reduced to the cerous state and free iodine liberated, which latter is determined by titration with thiosulphate. By this method cerium may be determined in the presence of thorium and the other members of the cerium group. This method is accurate to one-half per cent.

Grams cerium present.	Grams cerium found.	Error, gram.	Error, per cent.
0.22648	0.22697	0.00049	+0.2
0.22648	0.22657	0.00009	+0.04
0.22648	0.22697	0.00049	+0.2
0.22648	0.22752	0.00214	+0.5
0.22648 Ce. 0.4 $Th(NO_3)_4$	0.22737	0.00089	+0.4
0.11328 Ce. 0.10 $La_2(SO_4)_3$	0.11388	0.00060	+0.5

Analysis of a sample of "mischmetall" by the volumetric method showed a cerium content of 70.5 per cent.

Analysis of metallic cerium prepared in Run 1, above, showed the following composition:

Per cent. cerium.	Per cent. iron.
97.5	1.2
97.8	
97.8	

The determination of cerium by the gravimetric method in the cerium metal prepared in Run 4, above, showed 97.8 per cent. cerium.

Analysis of cerium cast into rods in an iron mold was as follows:

	Per cent.
Cerium	93.6
Iron	4.5
Insol. residue (oxide)	0.53
Magnesia (from MgO lining)	0.4
Carbon	0.88
Chlorine	0.07
	99.98

PURIFICATION OF METALLIC CERIUM.

The chief impurities of cerium (amounting in the aggregate to about two per cent.) obtained by the method previously described consisted of iron, cerium oxide and cerium carbide, of which over one per cent. was iron.

Owing to the fact that metallic cerium is but slowly attacked by concentrated sulphuric acid, filings of the metal were boiled with this acid. All of the iron was not dissolved, and the method is worthless for purification purposes.

The magnesium alloys of cerium, containing from 50 to 85 per cent. cerium, are brittle and may easily be pulverized to a fine powder. When digested with strong sulphuric acid for a few hours, the residue contains cerium, magnesium and iron. This method is also worthless.

The best method of purification consists in preparing the cerium amalgams. The amalgams are prepared by boiling mercury with cerium in a long iron pipe arranged with a condensing tube at the top. Solid amalgams are easily obtained by this method. The iron and impurities float to the top and may be skimmed off. The amalgams carefully prepared give only a very slight test for iron. The cerium and mercury may be separated by distilling the latter, but this must be done in a high vacuum to prevent oxidation of the cerium. A high temperature is required to drive off all the mercury. The amalgam should be placed in a magnesia vessel, and this in turn heated in an evacuated quartz vessel. The high temperature required would cause the collapse of an evacuated glass vessel.

PHYSICAL PROPERTIES OF METALLIC CERIUM.

In the determinations of the physical properties, metal of approximately 98 per cent. of cerium was used, unless otherwise specified.

1. *Atomic Weight.*—The atomic weight of cerium, determined from pure salts, is 140.25.

2. *Specific Gravity.*—The specific gravity determinations were made in a 50 cc. pyknometer of cylindrical form, with thermometer ground in central neck and with fused-in capillary tube at side. The liquids used were pure benzene and toluene, which have no chemical action on cerium. Several different specimens of metal were used for these determinations. The weight of metal taken varied from 3.4 to 11.2 grams. The average of determinations gave 6.92, at 25° C.

3. *Molecular State of Aggregation.*—No reference was found in the literature as to the crystallographic properties of cerium. Attempts were made by the writer to obtain crystals, but without success. The interior of many ingots of cerium were highly crystalline, especially in the center of blow-holes. The best condition for crystal growth is slow cooling from the molten condition. In order to aid the formation of crystals, a small quantity of cerium was melted under lithium chloride. The crucible was kept just hot enough to prevent the lithium chloride from solidifying, and was maintained at this temperature for several hours. The melting point of lithium chloride (about 550°) is somewhat below the melting point of cerium, and under these conditions the formation and growth of crystals would be expected. However, no definite crystals of cerium were obtained.

In order to examine the inner structure of cerium, photomicrographs of different specimens were made. The specimens were prepared by dry-polishing, and were etched with alcoholic HCl. An examination

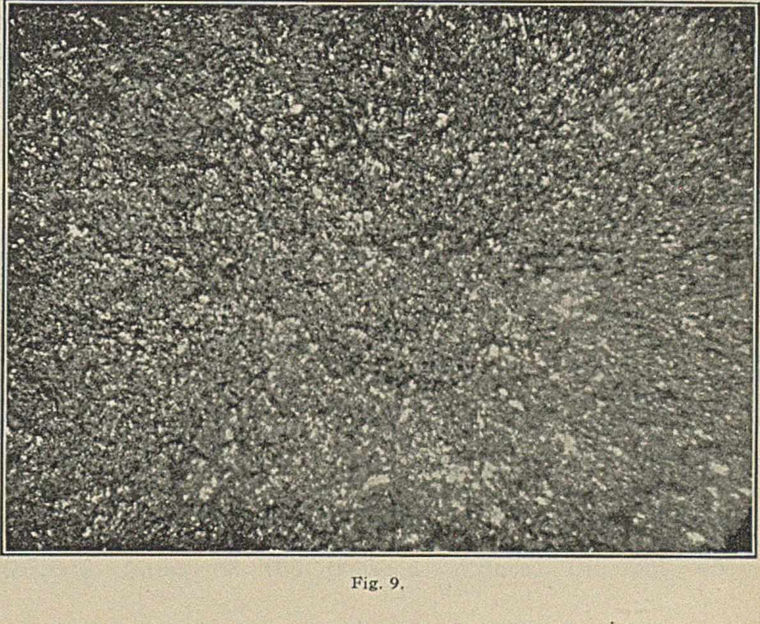

Fig. 9.

of these photomicrographs (see Fig. 9) shows homogeneity of structure.

4. *Hardness.*—For the determination of hardness the scleroscope was used. The hardness of cerium varies, depending upon whether the surface of the metal is rolled, freshly cut, or old. The average value of the hardness for rolled surface was 25.9. The average for freshly cut surface was 9.5. (The reading 100 is the hardness of the standard steel test plate.)

5. *Tenacity.*—Cerium is malleable and highly ductile. A strip of cerium was rolled to a thin sheet of a thickness of 0.015 mm. Cerium metal can easily be cut with a knife or scissors, and can be machined fairly well, although there is some tendency for the metal to buckle, as does lead.

6. *Electrical Conductivity.*—In order to make these measurements, a test bar was necessary. A good method of obtaining a known length and cross-section of metal is to take a short piece of capillary tubing, apply suction at one end, insert the other in the molten metal and so fill the tube. On account of the corrosive action of cerium on glass and silica, it was impossible to use this method.

It was difficult to cast cerium into solid rods, owing to its rapid oxidation in air. The following mold was prepared, which was so designed that molten cerium could quickly be poured into it from the melting crucible and oxidation prevented: A wrought-iron pipe, $^1/_4$ in. (0.65 cm.) inside diameter and about 5 in. (13 cm.) long, was screwed into the iron base. A piece of cast iron was turned on the lathe to the shape of a small funnel, and was screwed into the wrought-iron pipe. The cerium was melted in a magnesia-lined graphite crucible under a covering of fused salt. The mold was heated to a dull redness, and the entire contents of the crucible poured suddenly into the mold. Very little oxidation or burning of the metal occurred. A rod of cerium 3 in. (7.5 cm.) long was obtained. This metal contained 93.6 per cent. cerium and 4.5 per cent. iron. Although the inside of the pipe had been carefully cleaned, it was impossible to prevent contamination of the cast cerium with iron. As it was necessary to pre-heat the mold, a small amount of iron oxide necessarily formed, and, on contact with cerium, was reduced to metal and entered the rod as an impurity. The rod was turned down to size on the grinder.

The electrical conductivity measurements were made by the voltmeter-ammeter method. The potential drop was taken over one inch of test bar, and all measurements were made at room temperature. The current was varied from 6 to 18 amperes. The specific resistance of the sample was found to be 71.6 microhms per centimeter cube.

7. *Magnetic Properties.*—Stefan Meyer[46] has measured the magnetic susceptibility of many metals, among them that of cerium. He gives the atomic magnetic susceptibility of cerium ($K \times 10^{-6}$) equal to 34. He does not state the purity of the cerium used. The writer made no attempt to measure the magnetic susceptibility of cerium, but simply to determine if cerium is dia- or para-magnetic.

A small piece of cerium was suspended by a silk thread in a magnetic field of intensity about 5,000 lines per cubic centimeter. The metal so tested was paramagnetic, but not strongly so.

Cerium amalgam practically free from iron was sealed in a small glass tube and tested in a magnetic field. It was weakly but definitely paramagnetic. From these determinations it was concluded that pure cerium is paramagnetic.

8. *Melting Point.*—It was impossible to use the ordinary thermocouple method to determine the melting point, as no suitable protecting mantle could be found. Silica and porcelain are both attacked by cerium at its melting point. Magnesia, which is unattacked, is too porous a material for this purpose.

An attempt was made to obtain a cooling curve of cerium. About 60 grams of the metal were melted in a magnesia crucible in an electric resister furnace and readings were taken with a small copper-constantan couple placed in a porcelain mantle. It was thought that although the porcelain would be attacked somewhat, an approximate value for the melting point might be obtained. However, the cooling curve showed no constant temperature period and was worthless.

A small piece of cerium was attached to two long copper wires by means of small copper bolts and nuts, such as are used by watchmakers. Good electrical connection was obtained in this manner. The cerium was placed in a long Jena glass tube, sealed at one end and closed at the other by means of a rubber stopper, and so arranged that the tube could be evacuated. This was then placed in a tube furnace containing a calibrated thermocouple. A small amount of current was passed through the cerium, and when connection was severed, an electrical gong sounded. This scheme of obtaining the melting point did not work as the rubber stopper connection did not give a perfectly air-tight joint. The small amount of air in the tube combined with the cerium as the temperature increased. This caused a higher vacuum to be produced, with the result that more air entered the tube, and, upon subsequent repetition of this process, all the cerium was oxidized before the melting point was reached.

The approximate melting point was determined by heating a small quantity of cerium in a magnesia-lined graphite crucible and reading the temperature at which the metal softened by means of a thermocouple placed just above the metal. This crude method gave the approximate melting point as about 700°.

The real melting point of cerium was determined as follows: A small piece of cerium foil was fastened to two bent platinum wires by means of small copper bolts and nuts, and placed in a small glass bulb and the platinum wires sealed through the glass. The bulb was then evacuated by means of a mercury rotary pump, and sealed. A small incandescent lamp was connected in series with the cerium, which was heated in an electric muffle furnace. The temperature was read by a calibrated thermocouple. The melting point of the cerium was very definite, and occurred at a temperature of 635° C. The tube collapsed somewhat, but the method gave satisfactory results.

9. Ultimate Strength.—The same test bar was used for these determinations as in the electrical conductivity measurements. The ultimate strength was determined in an Olsen testing machine. The average diameter of the test bars was 0.212 in. (0.55 cm.). There was no elongation with constant load at 350 pounds (159 kg.). The test bar broke with a snap (like cast iron) at 495 pounds (225 kg.). The ultimate strength is equal to 12,900 pounds per square in. (9 kg. per sq. mm.).

10. Specific Heat.—The specific heat was determined in a Joly differential steam calorimeter. The principal difficulty encountered was to get a suitable method of protecting the cerium from attack by the steam. The cerium was sealed in a glass tube, but this method was unsatisfactory, owing to the time necessary for exchange of heat due to the small conductivity of the glass. Another method employed for protecting the cerium was to coat it with a mixture of amyl acetate in collodion. However, this coating was attacked by the steam and was liable to peel. The metal was also placed in a small nickel box, but was attacked by the steam. The best method of protecting cerium, at the same time allowing for rapid heat interchange, was to wrap the cerium tightly in several thicknesses of tinfoil. Blanks were run on copper and tin foil to check the accuracy of this calorimetric method. The value for the specific heat of copper obtained with this steam calorimeter was equal to 0.0925. The specific heat of cerium (20–100°) was measured and found equal to 0.0524. Mendeléeff[47] gives the specific heat of cerium equal to 0.05.

11. Heat Conductivity.—No measurements were made on the heat conductivity, and no references were found in the literature relative to this property. The heat conductivity seems to be fairly high, and, if so, cerium is probably one of the exceptional metals which has a low electrical conductivity and high thermal conductivity.

12. Latent Heat of Fusion.—From observations on melting cerium, the latent heat of fusion seems to be fairly high. It has not been determined to my knowledge.

13. Heat of Oxidation.—The heat of oxidation was determined in a Mahler bomb calorimeter. Cerium must not be burned in contact with platinum, as it will alloy with the latter. The cerium filings were placed in a small magnesia crucible in the calorimeter. From one to two grams of cerium filings were used for each determination, under an oxygen pressure of about fourteen atmospheres. The average value of the heat of oxidation was 1,740 calories per gram, or 60,900 calories per gram equivalent (CeO_2 = 243,600). These values are probably correct within 4 or 5 per cent. It is difficult to obtain an accurate value for the heat of oxidation where the products of combustion are non-volatile. The determinations in the case of cerium were unusually difficult to make, for the following reasons: The metal should be in a finely-divided form, but preferably in the shape of filings. When cerium is filed, care must be taken to prevent oxidation, owing to the low kindling point. A small amount of oxide forms in any case, and therefore makes the sample of metal taken non-uniform. If the filings are too coarse, oxide will fuse on the surface, and the metal in the interior will be unoxidized. Many of the difficulties encountered in the determination of the heat of oxidation of silicon[48] were met with here.

14. Single Potential.—Attempts were made to measure the single potential of cerium in the alcoholic solution of cerium chloride. No reliable measurement could be obtained, owing to the rapid formation of a film on the polished surface of the metal as soon as current flowed. The potential rapidly decreased as soon as the film appeared, which is almost instantaneous with the passage of current.

Measurements on the decomposition potential of the anhydrous mixed chlorides in absolute alcohol were made, using platinum electrodes. Gas was evolved at an applied electromotive force of 3.5 volts.

As the single potential of cerium could not be measured successfully, its value was calculated from the thermal data taken from Matignon's article on the anhydrous mixed chlorides:

Heat of formation of $CeCl_3$ (per 3Cl) = 270 calories
Heat of solution of $CeCl_3$ = 33 calories

The calculated decomposition potential of normal cerium chloride in aqueous solution is equal to 4.3 volts. Therefore the single potential of cerium in normal solution of its chloride measured against the normal calomel electrode is equal to —3.16 volts.

15. Thermo-electromotive Force.—Two small glass cells, protected by asbestos and fitted with wooden covers, were used. Standard thermometers with small stirrers attached were inserted through the cover. Cottonseed oil was used for the bath, and one of the cells was heated internally by means of several coils of resistance wire. The electromotive force was determined by the potentiometer method with a special piece of apparatus specially prepared for this kind of work. The thermo-electromotive force of cerium against copper is given in the table below and in the curve shown in Fig. 10. The current flowed at the hot junction from copper to cerium. The measurements are given in the following table:

Hot junction. Degrees C.	Cold junction Degrees C.	Electromotive force. Volt.
49.2	29.2	0.000075
100.0	25.0	0.000770
100.0	Red. to 30.0	0.000250
151.0	26.9	0.000399
151.0	Red. to 30.0	0.000387
200.5	29.7	0.000504
200.5	Red. to 30.0	0.000502

16. Optical Properties.—Cerium alone could not be used, owing to the fact that a thin film of oxide forms on the polished surface. Different alloys of cerium were tried, and the best ones for this purpose were found to be the magnesium-cerium alloys. The preparation of samples had to be done very carefully, as fine emery and rough entered the soft surface of the cerium. Dry-polishing with a very fine file (the finest obtainable) was the most satisfactory way of preparing the sample. For the methods of measurement of the optical properties the reader is referred to the article on the subject by Ingersoll and Littleton[49] on "A New Method of Determining the Optical Constants of Metals." The constants determined on the magnesium-cerium alloys are given in the table below:

Per cent. cerium.	n.	k.
83	1.60	1.74
61	1.43	2.30
26	0.73	4.79
Pure Mg	0.32	12.0

CHEMICAL PROPERTIES OF METALLIC CERIUM.

Metal of approximately 98 per cent. cerium content was used in these determinations.

Cerium is very slightly attacked by cold water, but in boiling water a slow evolution of hydrogen gas occurs and the metal is tarnished black. At room temperature the following solvents have no action on cerium: ethyl alcohol, amyl alcohol, chloroform, carbon tetrachloride, concentrated sulphuric acid, concentrated ammonium hydroxide, concentrated sodium hydroxide. Ethyl ether has a very slight action on the metal, as have also 3 per cent. and 30 per cent. hydrogen peroxide at room temperature. The action of dilute sulphuric acid, concentrated and dilute hydrochloric acid, concentrated and dilute nitric acid, in the cold, is moderately vigorous. Ammonium chloride and potassium chloride, at room temperature, have moderate action on the metal. This may be explained by the fact that in water a small amount of cerium hydroxide forms which is soluble in potassium chloride and ammonium chloride, thus causing fresh surface of the metal to be exposed and resulting in moderate attack of the metal by the solvent. At boiling temperature the following solvents did not attack the metal, chloroform, carbon tetrachloride, concentrated sulphuric acid, concentrated ammonium hydroxide. The metal was only slightly attacked by the following solvents at boiling temperature: ethyl alcohol, amyl alcohol, ethyl ether and concentrated sodium hydroxide. Dilute nitric acid, ammonium chloride, potassium chloride and 3 per cent. hydrogen peroxide at boiling temperatures gave moderate action. Dilute sulphuric acid, concentrated and dilute hydrochloric acid, concentrated nitric acid and 30 per cent. hydrogen peroxide gave vigorous evolution of gas at boiling temperature.

The action of various gases on cerium was studied. A small amount of cerium filings was placed in a porcelain boat in a hard glass tube. The air was displaced by the gas under test, and the tube heated gently by means of gas burners. The cerium filings heated in chlorine emitted a very bright light at a temperature of 210° to 215° C. The salt formed was tested and found to be anhydrous cerous chloride.

In bromine, cerium burned at a temperature of 215° to 220° C. with emission of less light than in the case of chlorine. The salt formed in solution in water, and was identified as the bromide.

In iodine vapors no light was emitted, although the tube was heated to a temperature of 300° C. On examination of the contents of the tube it was found that some iodide had formed.

Cerium burned with luminescence when heated in air to a temperature of 160° C. If a lump of cerium is sealed in a glass bottle and kept warm for some time, a black powder is seen to form upon the surface of the cerium, and when the bottle is opened this powder ignites at room temperature. This is probably due to the formation of a highly pyrophoric suboxide of cerium.

When cerium filings are heated to 345° in hydrogen gas, the hydride forms without emission of light. The hydride has been described and studied by Muthmann.[50]

Cerium filings were heated in nitrogen to a temperature of 1000° C. No luminescence was observed, but some nitride was formed. This nitride is a black powder, and has been studied and described by Matignon.[51]

When the nitride is heated in potassium hydroxide solution, evolution of ammonia gas occurs. When exposed to air the nitride gradually changes over to a brown oxide.

Cerium filings were heated in the vapors of sulphur. When the black substance which is formed is treated with dilute sulphuric acid, sulphuretted hydrogen is evolved. Cerium sulphide has been studied by various investigators.[52]

Cerium filings were heated to a temperature of 500° C. in an atmosphere of carbon monoxide. There was no visible reaction, but part of the filings appeared oxidized.

ALLOYS.

A number of different alloys of cerium were studied, and are described below. In most cases the alloys were high in cerium, usually containing about 70 per cent. cerium. The metals were weighed out in the proper proportions, using from five to ten grams of cerium. The cerium was first melted in a small porcelain crucible under a layer of sodium chloride, and the other metal added in small pieces. The porcelain crucible was, of course, attacked by the cerium, but it was found that a thin layer of silicide of cerium forms, and this protects the crucible from further attack. The metal can in most cases be removed without breaking the crucible if care is exercised, and therefore one crucible serves for several melts. The silicide does not appear as a contaminant in the alloy. Porcelain crucibles were used except in cases where especially pure metal was desired, when magnesia crucibles were employed.

The work on the alloys of cerium is presented below in an epitomized form. The time at the writer's disposal was such that a complete study of each alloy could not be made. However, specimens of all the alloys described have been preserved and will be used for future references.

Silver.—Silver alloys with cerium quietly, and the thermal change appears to be small. The alloy has a silvery-white luster, and is hard and brittle. From all appearances, a compound is probably formed between cerium and silver.

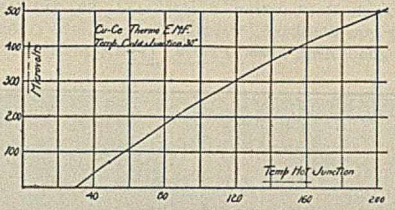

Fig. 10.

Gold.—When gold was added to molten cerium there was a slight flash from the crucible, but the reaction was not violent. The alloy was fairly soft, and had a reddish appearance. It disintegrated somewhat on aging, forming a purplish black powder.

Platinum.—The reaction between cerium and platinum appeared to be endothermic. The alloy was fairly hard and was pyrophoric. It disintegrated to a slight extent when aged.

Copper.—The cerium-copper alloy was hard and brittle, although the two component metals were soft and malleable. A compound is probably formed. The alloy disintegrated to a powder.

Tin.—This alloy was formed with the evolution of much heat. When first made, the alloy was pyrophoric, but on standing for a few months a powder formed, showing that the alloy disintegrated slowly when exposed to the air.

Antimony.—There was considerable evolution of heat on the formation of this alloy. The alloy was very soft and was non-pyrophoric. It did not oxidize nor disintegrate on aging.

Arsenic.—The reaction appeared to be exothermic. The alloy was fairly soft and somewhat pyrophoric. It did not decompose on being kept.

Carbon.—Carbon and cerium combine directly when heated together. The carbide has been referred to and described earlier in this article.

Silicon.—Cerium and silicon form the silicide $CeSi_2$. This compound may be formed by the reduction of the oxide of cerium. Large amounts of the mixed silicides have been prepared by the writer. The following mixture is recommended for their preparation:

	Grams.
M_3O_5	1,000
Powdered graphite	200
Powdered silicon	450

The silicide of cerium is somewhat brittle, and may easily be pulverized to a fine powder. It is a splendid reducing agent. When the silicide is added to cerium so that the silicon content is about 15 per cent. a good pyrophoric alloy is obtained.

Sulphur.—The preparation of the sulphide has been referred to earlier in this article.

Selenium.—Some reference is found in the literature to the selenide of cerium. Mosander reduced the selenite in a stream of hydrogen and obtained a brown substance of a disagreeable odor. Moissan has shown that the selenides may be obtained by the action of selenium fumes on cerium carbide.

Selium was added to molten cerium. The reaction was very vigorous, and was accompanied with the evolution of reddish fumes. The melt consisted of two portions, a powder and a metallic alloy. The powder was impure cerium selenide, and the alloy, which was pyrophoric, apparently consisted of the selenide dissolved in excess cerium.

Tellurium.—No reference was found in the literature to the telluride of cerium. Tellurium combined vigorously with molten cerium, giving a brownish pulverulent mass, which was probably the impure telluride. When treated with dilute acids, the well-known odor of hydrogen telluride was detected.

Lead.—When lead was added to molten cerium, a violet reaction occurred, causing a portion of the contents to be ejected from the crucible. The alloy was very soft, and emitted sparks of a reddish color when scratched with a file. The alloy disintegrated slightly on aging.

Calcium.—Calcium alloyed with cerium quietly, without evolution of much heat. The alloy was white and was harder than either constituent. When scratched with a file it emitted a cluster of bright sparks. It is stable in air, oxidizing very slowly. The alloy did not disintegrate.

Sodium.—Sodium alloyed with cerium quietly. The alloy was hard and slightly pyrophoric. It oxidized somewhat when exposed to air.

Aluminum.—Aluminum alloyed with cerium fairly quietly. The alloy was very hard and brittle. It disintegrated without oxidation. A compound of aluminum and cerium was probably formed. This alloy was not pyrophoric.

Zinc.—The combination of cerium and zinc was accompanied by a vigorous, in fact, almost explosive, reaction. There was a large amount of heat evolved. The alloy was hard, brittle and pyrophoric, and remained unoxidized when exposed to atmospheric conditions.

Cadmium.—Cadmium and cerium combined vigorously with considerable heat evolution. The alloy was hard, brittle and pyrophoric. On exposure to air a film of oxide formed slowly, but the alloy did not disintegrate.

Chromium.—The alloy was white in color, hard and brittle. It was somewhat pyrophoric. It remained unchanged in the air.

Manganese.—Manganese combined quietly with cerium, forming a fairly hard, pyrophoric alloy, stable in air.

Iron.—The iron-cerium alloys are very interesting, as they were the first pyrophoric alloys known, and were discovered by Dr. Auer von Welsbach. The alloys of about 70 per cent. cerium content are fairly hard and somewhat brittle. The microstructure of one of these alloys is shown in Fig. 11. It is seen that the structure is heterogenous, probably consisting in part of a cerium-iron compound. These alloys have been the subject of some discussion in the literature,[53] as have the reasons for the pyrophoric properties.[54] The writer believes that the question of the pyrophority depends upon the following factors: cerium alone is soft and malleable, and when scratched with a file, small particles are not broken off. However, when the alloy is hard and brittle, small particles are easily detached from the mass, and the friction is sufficient to raise the temperature of these small particles to the incandescent point of cerium (160°). As metallic compounds (such as Cu_3Sn) are as a rule hard and brittle, the addition of such compounds to cerium usually assures a pyrophoric alloy. The alloy should be high in cerium, so that ignition occurs at a low temperature, and should contain excess of cerium above that required for the formation of a compound (such as $CeSi_2$) to act as a binder and so prevent the disintegration of the alloy, as in the case of the cerium-aluminum alloy containing about 60 per cent. cerium.

Nickel.—The nickel-cerium alloys made were similar to the iron alloys, but were somewhat softer. The ones high in cerium were very pyrophoric.

Tungsten.—Powdered tungsten equivalent in weight to 15 per cent. was added to molten cerium. The tungsten dissolved fairly quickly and the reaction was quiet. The alloy was hard, brittle and pyrophoric.

Mercury.—Cerium forms amalgams fairly easily. Their preparation has already been described under the methods of purification. The amalgams containing only 1 or 2 per cent. of cerium are liquid, but the ones of higher percentage are solid. These amalgams oxidize easily in the air, and those containing 8 or 10 per cent. cerium take fire in the air.

Magnesium.—The whole series of these alloys were prepared, and have been discussed under optical properties. The alloy containing about 83 per cent. cerium is highly pyrophoric. Most of these alloys are brittle and can be easily pulverized. Excellent flashlight powders can be prepared from the ones of higher cerium content. These alloys also form splendid reducing agents, as the combination of cerium and magnesium is an endothermic reaction, and when the alloy is oxidized, more heat is emitted than from an equivalent mechanical mixture of the two constituents. The fact that the alloys of from 60 to 75 per cent. cerium content may be easily pulverized in a mortar to a fineness of 200 mesh should render these alloys valuable for thermal reductions. A small amount of metallic vanadium was prepared by reducing V_2O_5 by this method. The alloys of from 75 to 85 per cent. cerium content can be pulverized, but they are so highly pyrophoric that it is difficult to prevent igniting them.

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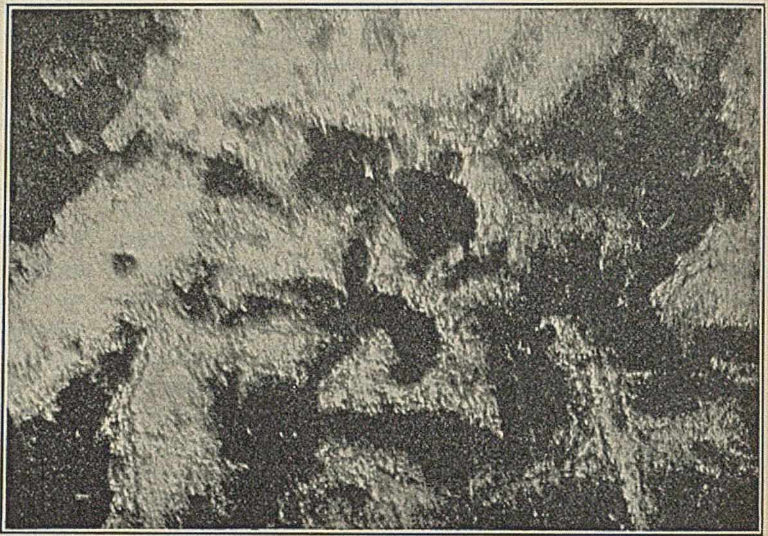

Fig. 11.

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53. (*c*) C. R. Behm, *Ibid.*, **34**, 361, 367 (1910).
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ON THE DENSITY OF SILICATE MIXTURES.

By Edwin Ward Tillotson, Jr.

Received October 20, 1911.

It has been shown by Winkelmann and Schott[1] that the densities of a glass may be calculated, with a rough degree of accuracy, from its chemical composition. The method depends upon the supposition that the several glass-forming oxides have densities which are always the same, for a particular oxide, in whatever combination it occurs. On this assumption, by addition of the partial volumes of the oxides, the densities of the glasses were calculated, according to the following equation,

$$(1)\quad \frac{a_1}{z_1}+\frac{a_2}{a_2}+\frac{a_3}{z_3}=\frac{100}{S},$$

where S is the density of the glass, a_1, a_2, a_3 are the percentages of the oxides, and z_1, z_2, z_3 are the densities of the oxides in the glass.

That this assumption is not entirely fulfilled is shown in the original article by the values of the densities for twenty-nine glasses calculated by this method. However, the average variation of 1½ per cent., between the observed and calculated values does not militate against the methods value where extreme accuracy is not required.

In order that the factors used by Winkelmann might be checked against the more recent and accurate work in pure silicates, they were employed in calculating the densities of a series of calcium and magnesium metasilicates, described by Larsen,[2] two series of lithium-barium and lithium-calcium metasilicates, described by Wallace,[3] and some mixed feldspars prepared by Day and Allen.[4]

The observed and calculated densities of the calcium-magnesium silicates are given in Table I. It is evident from these figures that Winkelmann's factors gave a fair value for the density of magnesium silicate, but a false value for calcium silicate. This is shown graphically in Line II (Fig. 1). The observed density of calcium silicate is greater than that of magnesium silicate while the hypothetical, calculated, density of calcium silicate is less. New factors for CaO and MgO were then calculated from the values of the observed densities. Following are the two sets of factors which were employed:

	Winkelmann.	Modified.
SiO_2	2.3	2.3
CaO	3.3	4.1
MgO	3.8	4.0

The densities of the several calcium-magnesium silicates computed with the aid of the modified factors are given in the last column of Table I and shown graphically in line I (Fig. 1). They show a far more satisfactory agreement with the observed densities, and since the errors throughout the entire series are less than one-half of one per cent., the densities assumed for the oxides in the glass may be considered to be nearly correct.

Table I.—$CaOSiO_3$-$MgSiO_3$.

$CaSiO_3$, per cent.	CaO, per cent.	MgO, per cent.	SiO_2, per cent.	Density. Obs.[1]	Calc.[2]	Calc.[3]
100	48.20	00.00	51.80	2.904	2.698	2.920
95	45.80	2.01	52.19	2.899	2.700	2.910
85.26	41.09	5.91	53.00	2.891	2.701	2.897
74	35.70	10.43	53.87	2.881	2.706	2.879
64	30.84	14.43	54.73	2.872	2.709	2.863
60	28.92	16.04	55.04	2.859	2.711	2.855
53.64	25.85	18.59	55.56	2.854	2.713	2.848
40	19.28	24.06	56.66	2.834	2.718	2.829
30	14.46	28.07	57.47	2.821	2.722	2.815
10	4.82	36.09	59.09	2.780	2.730	2.787
5	2.41	38.10	59.49	2.777	2.733	2.780
0	0.00	40.10	59.90	2.758	2.735	2.773

When these factors were used for calculating the densities of some of the Jena glasses, the results were, in general, more satisfactory than those obtained with Winkelmann's factors. The following examples show the observed and calculated densities of several of these glasses.[4]

No.	Density. Obs.	Calc.[2]	Calc.[3]	Error.[2] Per cent.	Error.[3] Per cent.
3	2.424	2.42	2.424	0.2	0.0
6	2.585	2.52	2.543	2.5	1.6
10	2.518	2.51	2.545	0.3	1.0
34	2.378	2.34	2.350	1.6	1.2
			Average,	1.15	0.95

The observed and calculated densities of the lithium-barium metasilicates and the lithium-calcium metasilicates are given in Tables II and III respectively and all shown graphically in Fig. 2. In his original communication Winkelmann gave no factor for lithium oxide, consequently the value employed in

Table II.—Li_2SiO_3-$BaSiO_3$.

$BaSiO_3$. Per cent.	Li_2O. Per cent.	BaO. Per cent.	SiO_2. Per cent.	Density. Observed.[5]	Calc.[3]
0	33.30	00.00	66.70	2.61	2.63
10	29.97	7.18	62.85	2.70	2.74
20	26.64	14.36	59.00	2.80	2.87
30	23.31	21.53	55.16	2.91	3.00
40	19.98	28.71	51.31	3.17	3.14
50	16.65	35.89	47.46	3.38	3.31
60	13.32	43.06	43.62	3.50	3.48
70	9.99	50.24	39.77	3.77	3.69
80	6.66	57.42	35.92	4.02	3.91
90	3.33	64.60	32.07	4.19	4.16
100	0.00	71.78	28.22	4.44	4.44

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[1] Winkelmann, *Ann. d. Phys. und Chem.*, **49**, 401 (1893); Winkelmann and Schott, *Ibid.*, **51**, 697 (1894); "Jena Glass and Its Industrial Applications," Hovestadt (English edition), p. 148.

[2] *Am. J. Sci.*, **28**, 263 (1909).

[3] *Z. anorg. Chem.*, **63**, 1 (1909).

[4] *Bull.* **31**, Carnegie Institute of Washington.

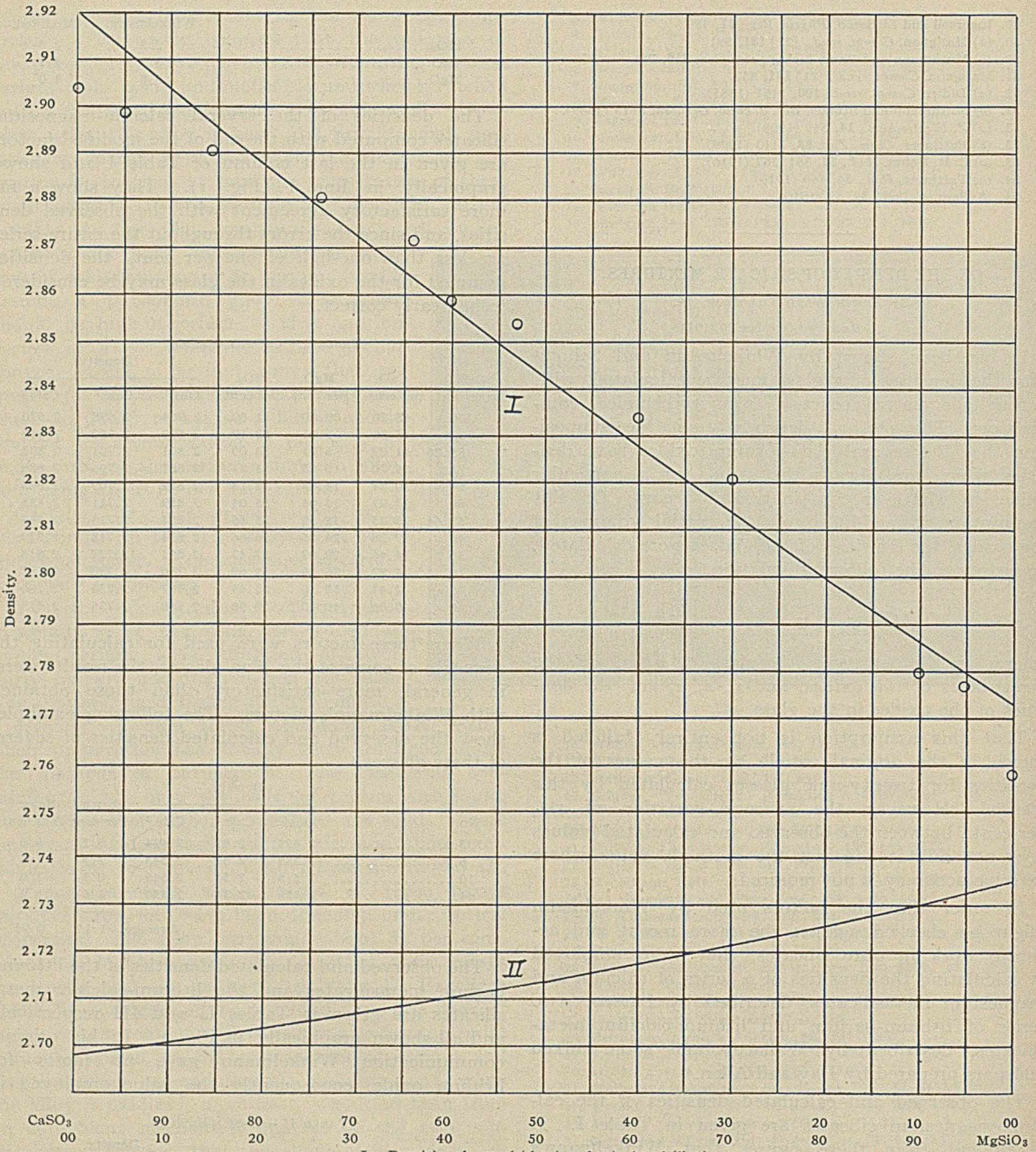
[1] Larsen, *Am. J. Sci.*, **28**, 263 (1909).

[2] Using Winkelmann's factors.

[3] Using modified factors.

[4] Winkelmann and Schott, *Loc. cit.*

[5] Wallace, *Z. anorg. Chem.*, **63**, 1 (1909).



I. Densities observed (dots) and calculated (line).
II. Densities calculated from Winkelmann's factors.
Fig. 1.

TABLE III.—Li_2SiO_3-$CaSiO_3$.

$CaSiO_3$. Per cent.	Li_2O. Per cent.	CaO. Per cent.	SiO_2. Per cent.	Density. Obs.[1]	Calc.[2]	Calc.[3]
0	33.30	00.00	66.70	2.61	2.63	2.63
10	29.97	4.82	65.21	2.64	2.63	2.65
20	26.64	9.64	63.72	2.69	2.645	2.69
30	23.31	14.46	62.23	2.72	2.655	2.71
40	19.98	19.28	60.74	2.76	2.66	2.74
50	16.65	24.10	59.25	2.80	2.665	2.77
60	13.32	28.92	57.76	2.80	2.67	2.80
70	9.99	33.74	56.27	2.84	2.68	2.83
80	6.66	38.56	54.78	2.85	2.69	2.85
90	3.33	43.38	53.29	2.88	2.69	2.88
100	0.00	48.20	51.80	2.91	2.70	2.92

these calculations is new so far as the writer is aware. The factors used in computing these densities are as follows:

	Winkelmann.	Modified.
SiO_2	2.3	2.3
BaO	7.0	7.0
CaO	3.3	4.1
Li_2O	...	3.7

In the case of the lithium-barium series, Winkelmann's factor for BaO was found to give good results,

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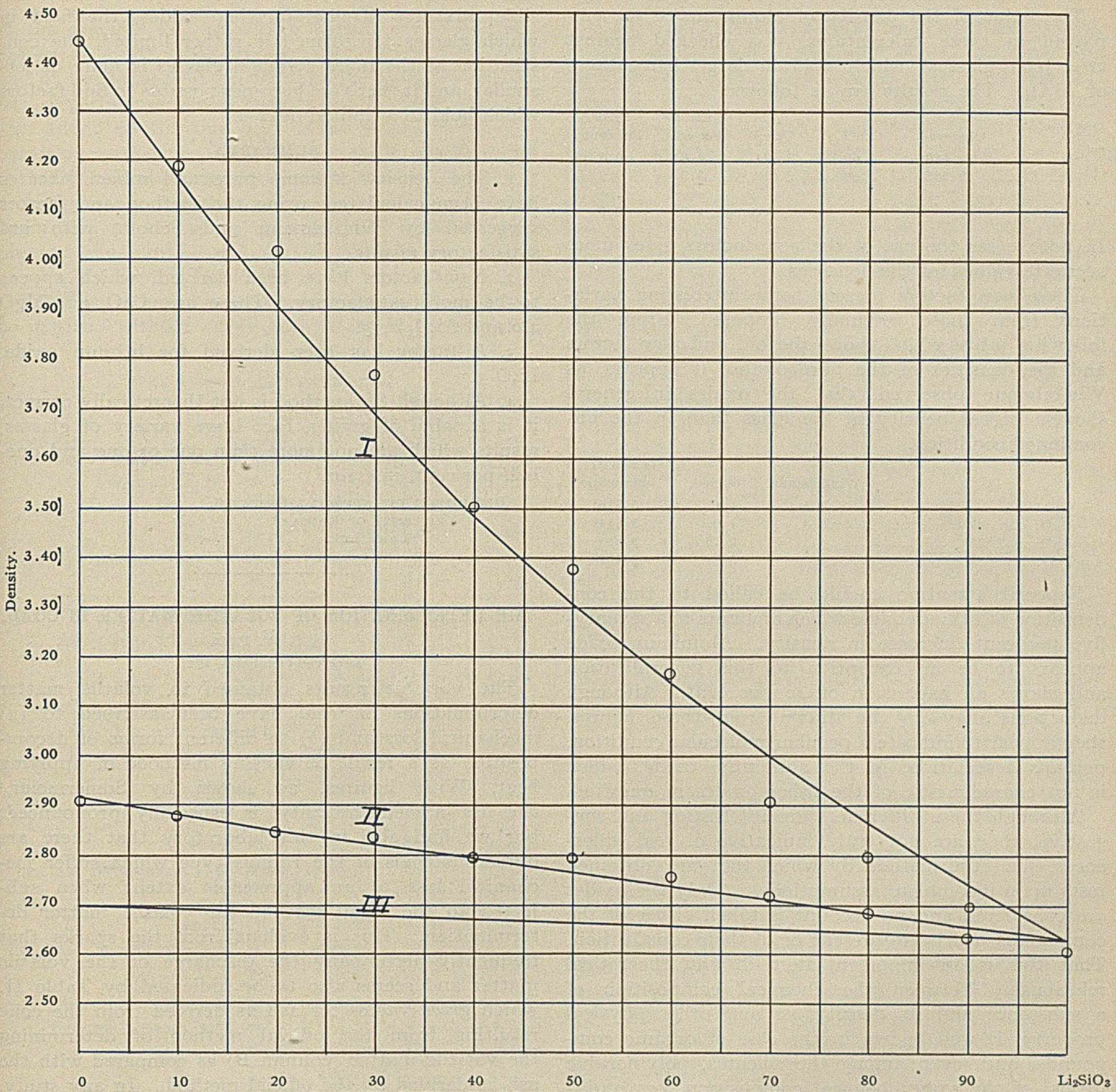
[1] Wallace, *Z. anorg. Chem.*, **63**, 1 (1909).

[2] Using Winkelmann's factors.

[3] Using modified factors.



I. $BaSiO_3$–Li_2SiO_3—Densities observed (dots) and calculated (line).
II. $CaSiO_3$–Li_2SiO_3—Densities observed (dots) and calculated (line).
III. Density calculated from Winkelmann's factors.

Fig. 2.

and was employed in the calculations. The error between the observed and calculated values of the density was comparatively large, however, but did not exceed in average of one and one-half per cent. A much better agreement exists between the observed and calculated densities of the lithium-calcium silicates. In this case the average error is less than one-half of one per cent., and is doubtless as satisfactory as could be expected of the method.

In Table IV is recorded a similar comparison of the observed and computed densities of several mixtures of albite and anorthite.[1] From the values given in this table, it is evident that the densities employed by Winkelmann give false results. The figures given in the last two columns of Table IV were calculated with the aid of the following factors:

TABLE IV.—ALBITE-ANORTHITE.

					Density.		
	SiO_2.	Al_2O_3.	CaO.	Na_2O.	Obs.[1]	Calc.[2]	Calc.[3]
An...........	43.33	36.60	20.06	0.11	2.700	2.980	2.700
An_5Ab........	47.10	34.38	17.00	1.74	2.648	2.880	2.644
An_2Ab........	51.06	31.72	13.65	3.68	2.590	2.820	2.600
An_1Ab_2.......	60.01	25.24	7.09	7.79	2.486	2.680	2.497

	Winkelmann's.	Modified.
SiO_2...........................	2.3	2.3
Al_2O_3.........................	4.1	2.75
CaO...............................	3.3	4.1
Na_2O...........................	2.6	2.6

[1] Day and Allen, *Loc. cit.*

[2] Using Winkelmann's factors.

[3] Using modified factors.

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[1] Day and Allen, *Loc. cit.*

The value of the density of aluminum oxide, employed in these calculations, was checked against two Jena glasses[1] which contain large percentages of Al_2O_3. The results are as follows:

No.	Observed.	Calc.[2]	Calc.[3]	Error.[2] Per cent.	Error.[3] Per cent.
4	2.480	2.60	2.471	4.8	0.3
9	2.588	2.69	2.612	3.9	0.9
			Average,	4.35	0.6

In both cases the use of the new factors gives more accurate values for the densities.

These new factors present some interesting variations from those originally proposed. From the following table, which shows the old and new factors and the densities of the pure oxides, it appears, as Winkelmann observed, that the oxides in general show a higher density in the glass than in the uncombined condition.

	Winkelmann.	Modified.	Density of pure oxide.
CaO	3.3	4.1	3.316[4]
MgO	3.8	4.0	3.614[5]
Al_2O_3	4.1	2.75	3.85[6]
Li_2O	...	3.7	2.102[6]

Especial attention should be called to the condensation of lithium oxide which amounts to a seventy-five per cent. increase in density. Aluminum oxide appears to be an exception to this generalization and shows an expansion of 40 per cent. Although deductions may not be drawn from these figures, they appear to indicate a peculiar molecular condition, perhaps association, in the aluminum oxide, which is not characteristic of the other oxides in question.

Although these differences are interesting and suggestive, they are not truly indicative of real differences, since the method by which they are obtained rests upon incomplete assumptions. Only the oxides are considered and no account is taken either of the compounds which are present or of their constitution. That this is an important item in any theoretical relationship between the chemical composition of a substance and its density, or any other physical property, is well known in the case of organic compounds, and, even among the silicates, polymorphic forms[7] of the same chemical composition, but of different density, have been described. A knowledge of the different compounds which exist, together with knowledge of the compounds which are stable at the temperature at which the glass may be formed, will aid materially in solving the numerical relationship between the chemical composition of a glass and its density. Until such information is at hand resort must be had to empirical factors which represent not the true density, but the true density plus or minus an element which is characteristic of the nature of the compound which is formed. Since, in all the possible mixtures of glass-forming oxides, the field in which glasses are formed is rather limited, the constitution of the more common glasses is more or less similar, and it therefore becomes possible to find factors which hold to a limited degree.

SUMMARY.

1. The density of some pure and mixed silicates have been calculated, using the method and factors suggested by Winkelmann and Schott, with unsatisfactory results.

2. New factors have been derived, which appear to be more satisfactory. These are CaO 4.1, MgO 4.0 and Al_2O_3 2.75.

3. A factor has been derived for lithium oxide, Li_2O 3.7.

4. Although the method is not theoretically correct, it is capable of giving, for large variety of glasses, results which are not more than one or one and one-half per cent. in error.

Department of Industrial Research,
University of Kansas.
Lawrence.

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[1] Winkelmann and Schott. *Loc. cit.*

[2] Using Winkelmann's factors.

[3] Using modified factors.

[4] Day and Shepherd, *Am. J. Sci.*, [4] **22**, 265 (1906).

[5] Larsen, *Ibid.*, [4] **28**, 273 (1909).

[6] Van Nostrand's Chemical Annual.

[7] "The Lime-silica Series of Minerals," Day and Shepherd, *J. Am. Chem. Soc.*, **28**, 1089 (1906). "Minerals of the Composition $MgSiO_3$; A Case of Tetramorphism," Allen, Wright and Clement, *Am. J. Sci.*, [4] **22**, 385 (1906).

THE DETERMINATION OF VOLATILE MATTER IN COAL.

By S. W. Parr.

Received October 6, 1911.

The variable results obtained in volatile matter determinations on coal have been ascribed to (*a*) mechanical loss and (*b*) to different forms of decomposition as a result of varying methods of applying heat. With lignites, as shown by Somermeier,[1] the first-named difficulty is especially pronounced; but we find also in this laboratory that there are numerous coals of the Illinois type which suffer mechanical loss to an appreciable extent when subjected to the usual method for volatile matter determination. This is evident from the sparks that frequently accompany the discharge of the volatile matter and seems also to be indicated by Table II, which gives values for ash as derived from the coke resulting from the official method of determining the volatile matter (column B) as compared with the ash as derived by the official method. In any study, therefore, of the effect of varying temperatures, it is essential that variations due to mechanical loss be first eliminated before conclusions can be safely drawn as to the effect of varying degrees of heat. Moreover, the method employed must admit of the application of the maximum of heat in the minimum space of time in order that variations due to different sorts of decomposition may be brought within a narrow range. This precludes, of course, the application of a slow preliminary heating as suggested for lignites, at least with Illinois coals.

In our experiments it has seemed well to bear in mind certain other sources of variation. First on account of the great avidity of freshly mined coal for oxygen, it is possible that this element, mechanically held or absorbed by the finely ground material, accentuates or adds to the normal content of oxygen

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[1] *J. Am Chem. Soc.*, **28**, 1003 (1906).

of the crucible and may thus furnish an initial oxidation of appreciable amount. To guard this point and at the same time prevent mechanical loss, numerous experiments were undertaken wherein a liquid was added to the dry coal which would have non-oxidizing properties and whose vapor would tend to carry out the oxygen content of the crucible at a temperature below that where oxidation would begin and at the same time promote adhesion and prevent the blowing out of the particles as a result of the moistening throughout of the mass. Such a liquid, of course, must be completely volatile and be distilled without decomposition by the subsequent heat.

Table I.—Volatile Matter in Coal.

Table No.	Lab. No.	Kind of coal.	A. Standard method.	Variation + or — from av., Column A.	B. Standard with kerosene.	Variation + or — from av., Column B.
1	117	Vermilion Co., Ill.	38.90	+0.21	38.40	+0.07
			38.48	—0.21	38.26	—0.07
		Average,	38.69	0.21	38.33	0.07
2	128	Saline Co., Ill.	36.41	—0.14	36.61	—0.03
			36.69	+0.14	36.68	+0.04
		Average,	36.55	0.14	36.64	0.03
3	214	Lignite, Mississippi.	47.09	+1.06	44.87	+0.58
			45.70	—0.33	44.35	+0.06
			45.25	—0.78	43.95	—0.34
			46.09	+0.06	43.99	—0.30
		Average,	46.03	1.11	44.29	0.64
4	1762	Sangamon Co., Ill.	40.48	—0.74	40.05	+0.01
			41.72	+0.50	40.03	—0.01
			41.67	+0.45	..	..
			41.00	—0.22	..	..
		Average,	41.22	0.95	40.04	0.01
5	1809	Williamson Co., Ill.	37.24	+0.03	37.41	—0.05
			37.18	—0.03	37.52	+0.06
		Average,	37.21	0.03	37.46	0.05
6	1810	Franklin Co., Ill.	34.65	—0.32	34.78	+0.10
			35.30	+0.33	34.59	—0.09
		Average,	34.97	0.32	34.68	0.09
7	1870	Christian Co., Ill.	41.12	+0.68	39.41	+0.10
			39.76	—0.68	39.21	—0.10
		Average,	40.44	0.68	39.31	0.10
8	1878	Jackson Co., Ill.	34.32	—0.12	34.72	+0.19
			34.55	+0.11	34.70	+0.17
			..	..	34.43	—0.10
			..	..	34.26	—0.27
		Average,	34.42	0.11	34.53	0.36
9	2902	Williamson Co., Ill.	33.29	—0.18	33.78	0.00
			33.65	+0.18	33.77	0.00
		Average,	33.47	0.18	33.77	0.00
10	4035	Sangamon Co., Ill.	40.47	+0.07	41.35	+0.01
			41.33	—0.07	41.33	—0.01
		Average,	41.40	0.07	41.34	0.01
11	4085	Vermilion Co., Ill.	35.85	—0.08	36.54	—0.04
			36.01	+0.08	36.63	+0.05
		Average,	36.93	0.08	36.58	0.04
12	4130	Franklin Co., Ill.	37.06	+0.05	36.72	+0.16
			36.96	—0.05	36.41	—0.15
		Average,	37.01	0.05	36.56	0.15
		Average variation,		0.33		0.13

Numerous vehicles were tried, such as ether, alcohol, carbon tetrachloride, petroleum ether, kerosene, etc. Of these substances, kerosene seemed to be the best adapted, besides being readily available. The procedure was very simple. One gram of the air-dried sample, ground to 80 mesh, was weighed into the crucible and ordinary kerosene, from 10 to 15 drops, added, sufficient in amount to completely penetrate and saturate the coal. The cover was then put in place, the crucible supported on a platinum or nichrome triangle and placed directly in the usual Bunsen flame, 20 cm. high as prescribed by the Committee on Coal Analysis.

The results of a number of determinations are given in Table I, along with results obtained by the official method.

The values at the foot of the columns indicated that by the use of kerosene the variations are reduced from an average of 0.33 per cent. to 0.13 per cent.

As further evidence tending to show absence of mechanical loss when kerosene is applied, the results in Table II show the ash as obtained by the official method in column A, with which may be compared column C, showing the results for ash as derived from the coke obtained when kerosene was added as above described.

Table II.—Mechanical Loss as Indicated by Ash Determinations.

Table No.	Lab. No.	Kind of coal.	A. Ash by official method.	B. Ash from coke residue by official method.	C. Ash from coke residue using kerosene.
1	117	Vermilion Co., Ill.	8.74	8.66	8.82
2	1162	Christian Co., Ill.	11.32	11.15	11.26
3	2902	Williamson Co., Ill.	10.12	9.75	10.07
4	2952	Pittsburg, Pa.	16.95	16.92	16.89
5	4035	Sangamon Co., Ill.	9.44	9.31	9.40
6	4085	Vermilion Co., Ill.	23.58	23.70	23.50
7	4130	Franklin Co., Ill.	4.87	4.79	4.80

It seems fair to conclude, therefore, that an advantage attends the use of kerosene and that the matter of mechanical loss is thereby eliminated. This brings us to a consideration of that phase of the matter which relates to variations due to differences in the application of heat. Fieldner and Davis[1] have shown that variations in heat as derived from burners of different sizes, different types of gas, etc., yield different values. Their discussion of the results would lead one to infer that in their opinion the various temperatures employed produced a varying speed of decomposition which resulted in the fixation of varying amounts of carbon. With bituminous coals at least it would seem essential to first eliminate the possibility of mechanical loss. But, aside from this feature of the case, there are many evidences that in the main the variations due to different temperatures are the result of a more or less complete driving off of the residual hydrogen, to variations in the amount of carbon deposit on lid and sides of the crucible, to the oxidizing or reducing character of the flame immediately above and around the lid of the crucible, the extent of leakage or care with which the lid of the crucible is made to fit, etc.

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[1] This Journal, **2**, 304 (1910).

Further uniformity of results might be expected if we could locate more precisely the point wherein the variation occurs. This feature of the case is receiving further study.

As bearing somewhat on the case, the following table is submitted. If any interpretation can be attempted from these results it would seem to be that the higher results are not always to be credited to the larger burner and the higher temperature. It is more likely that coals vary as to the ease or completeness with which they part with their last residuum of gas.

I am indebted to Mr. F. W. Whittum and Mr. J. M. Lindgren for the analytical results accompanying this paper.

TABLE III.

Table No.	Lab. No.	Kind of coal.	A. Standard method with kerosene, Sargent burner.	B. Standard method with kerosene, Fletcher burner.	B compared with A variation + or —.
1	117	Vermilion Co., Ill.	38.33	39.44	+1.11
2	128	Saline Co., Ill.	36.64	37.11	+0.47
3	214	Lignite, Mississippi.	44.29	44.35	+0.06
4	1762	Sangamon Co., Ill.	40.04	39.84	—0.20
5	1809	Williamson Co., Ill.	37.46	37.78	+0.32
6	1810	Franklin Co., Ill.	34.68	35.18	+0.50
7	1870	Christian Co., Ill.	39.31	39.65	+0.34
8	1878	Jackson Co., Ill.	34.53	34.22	—0.31
9	2902	Williamson Co., Ill.	33.77	34.16	+0.39
10	4083	Vermilion Co., Ill.	36.58	36.29	—0.29
11	4130	Franklin Co., Ill.	36.56	36.99	+0.43

In column A, the burner used is illustrated as No. 1000 in Sargent's catalogue. It has an internal diameter of 9 mm.

In column B, the Fletcher burner had an internal diameter of 11 mm.

UNIVERSITY OF ILLINOIS,
URBANA.

SOME NEW FEATURES IN THE ELECTROLYTIC DETERMINATION OF LEAD.

By JOHN G. FAIRCHILD.

Received Sept. 28, 1911.

It has been found that good deposits of lead peroxide, free from flakes and of close texture, can be obtained on a smooth platinum cylinder in two hours' time without rotation, and as much as 100–200 mg. in weight. This can be raised to 300 mg. but there is danger of flaking off. The secret of success is a low amperage to begin with and a hot solution, 50°–60° C.

For alloys high in lead two grams or more are weighed out and an aliquot taken to represent about 0.1 gram of metallic lead. The volume of electrolyte is 200 cc. in a 250 cc. beaker, and contains 30 cc. strong HNO_3. Heat to 50°–60° C., using an anode of 25 sq. in. surface with a cathode cylinder of 12 sq. in. The anode should be burnished frequently and ignited previous to placing in the electrolyte. This ignition removes any greasy film adhering to the cylinder. Split cover glasses are used to prevent loss through evaporation of the hot solution, which just completely immerses the edge of the anode cylinder. The current is started at 0.25 am. for one hour and a half when it is raised to 0.5 am. for half an hour longer to remove the last traces of lead, and the cover glasses are rinsed down. At the end of two hours deposition is complete, as shown by the newly immersed stem remaining bright. The beaker is lowered and removed, being replaced by one containing clean water for rinsing the cylinders, which are then disconnected, the anode being rinsed in a glass of alcohol, drawn through a flame to burn off what adheres while holding the cylinder in a vertical position. It is then held for a few seconds about a foot above the flame to dry thoroughly, and weighed. On adding ammonia to the electrolyte and passing H_2S, no more than a mere brownish color should show.

To prove the accuracy of this method, purified lead sulphate was taken as the standard. An amount equal to 0.7335 gram was put into a 500 cc. flask and dissolved in just enough hot am. acetate solution, 100 cc. being taken for analysis by means of a pipette standardized to the flask. After adding 30 cc. HNO_3 of 1.42 sp. gr., this aliquot was made up to 200 cc. The electrolyte is best kept hot throughout the run by means of a hot plate or burner. The results for lead sulphate and test lead were as follows:

$PbSO_4$.	PbO_2 equiv.	PbO_2 found.	Pb. Per cent.[1]
0.1467	0.1157	0.1156	99.92
0.1467	0.1157	0.1160	100.26
0.1467	0.1157	0.1155	99.83
0.1467	0.1157	0.1159	100.17
Test lead.			
0.1000	0.1157	0.1145	98.92
0.1000	0.1157	0.1143	98.72
0.1000	0.1157	0.1142	98.63
0.1000	0.1157	0.1147	99.14
0.1000	0.1157	0.1145	98.92
0.1000	0.1157	0.1146	99.04

Whenever a weight was low the lead was found to be not all deposited, due to faulty manipulation which is not likely to occur. If the electrodes short-circuit re-solution occurs with some lead flaking off.

Lead scrap and furnace dross can be treated thus: About 5 grams are dissolved in $HNO_3 + H_2SO_4$ in a Kjeldahl flask and evaporated till fumes appear. After cooling, the impure $PbSO_4$ is filtered off, the paper punctured and the precipitate rinsed back into the flask. It is then treated with just sufficient hot saturated am. acetate solution, which is warmed till solution is complete, then filtered into a 500 cc. flask, a proper portion being taken for electrolysis.

On comparison with pure lead it will be seen that material relatively low in lead will require only about half an hour at 0.5 am., a small percentage of lead being given a higher amperage. In this way can lead be readily separated from copper, manganese, silver, antimony, etc.? When a relatively large amount of copper is present, as in blister copper, only 20 cc. nitric acid may be present. The presence or absence of am. nitrate seemed to have no effort on the results.

This method gives lower results than the chromate method; thus, by the latter 59.25 per cent. lead was

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[1] Conversion factor 0.866.

found in a lead dross, by the electrolytic 58.85 per cent. On a copper matte high in lead, the figures gave 10.57 chromate, 10.32 electrolytic.

Material such as a copper matte can be dissolved in HNO_3, the sulphur globule oxidized by adding $KClO_3$ crystals, then heated with H_2SO_4 till fumes come off.

The voltage of the hot solution is 2–2.5 volts. A straight platinum wire was first tried as cathode but metallic lead deposited on it. Also, with 1 ampere of current metallic lead deposits on the cathode. Even with a weak current in a cold solution there is danger of metallic lead separating. Results are best obtained with a low voltage and low current density.

In the early experiments, whenever lead sulphate was involved, this was changed to carbonate by digestion with ammonium carbonate, and the lead carbonate was dissolved in dilute nitric acid. These steps were soon found to be unnecessary, the simple solution of the lead sulphate in am. acetate greatly shortening the method.

U. S. Geological Survey,
Washington, D. C.

NAPHTHALENE IN ROAD TARS. I. THE EFFECT OF NAPHTHALENE UPON THE CONSISTENCY OF REFINED TARS.

By Prevost Hubbard and C. N. Draper.

Received November 6, 1911.

Naphthalene, $C_{10}H_8$, often occurs in coal tar in larger quantities than any other one hydrocarbon and for this reason it is natural to suppose that it exerts an appreciable influence upon the quality and applicability of coal tars used as road binders. In this country the use of tars in road treatment and construction has advanced rapidly during the past few years and upon the market to-day are to be found a number of tar preparations intended for such use. These preparations are as a rule made by distilling off the lighter and more volatile constituents from both crude coal tar and crude water-gas tar or mixtures of the two. The residual products, which vary in consistency according to the extent and method of distillation, are sold for road purposes. Many successes and many failures have resulted from the use of coal tar and water-gas tar road binders, and often no clew has been obtainable as to the reason for such diverse results. In view of this fact, a systematic study of the principal chemical constituents of road-tar preparations and their effect upon the quality of such preparations is now being made in the laboratories of the Office of Public Roads, United States Department of Agriculture.

In the present paper, which is the first of a series upon naphthalene, no attempt will be made to review the chemistry of this substance, since this discussion is reserved for a later publication which will cover the entire subject as presented in the individual papers. A few remarks concerning certain physical properties of naphthalene may, however, not be amiss at this point.

Naphthalene, in the pure state, exists in white crystalline masses of thin rhomboidal scales melting at 79° C. and having a boiling point of 218° C. Its specific gravity at 15° C. is 1.1517. It has a very characteristic odor, commonly familiar in moth balls, and is extremely volatile, considering its high molecular weight, so much so that in the manufacture of coal gas it is only partially deposited in the condensers, while the remainder is carried into the purifiers and into the gas mains, where it deposits in the bends of pipes during cold weather and often causes them to become clogged. Naphthalene volatilizes far below its boiling point and, in crude tars, distils to a considerable extent with aqueous vapor and also with the light tar oils, which accounts for its occurrence in the first fractions. Even at ordinary temperatures, it volatilizes slowly and gives off a penetrating tarry odor. It is slightly soluble in hot water, but dissolves easily in alcohol, ether, fatty and essential oils, acetic acid, and especially in the phenols and lighter tar distillates. No entirely satisfactory method for the quantitative determination of naphthalene in tar has, as far as the authors are aware, been devised up to the present time, although methods have been put forth by various investigators for the determination of naphthalene in illuminating gas.

It is a rather generally accepted theory that, in the manufacture of coal gas, the formation of naphthalene is due to certain complex reactions which take place only at the high temperatures at which the retort is maintained in modern gas-house practice. According to Cooper,[1] "a few years ago—when lower temperatures were in vogue, and when lower makes per ton of coal carbonized were registered—naphthalene was an almost unknown quantity; but now that the stress of competition demands the highest possible output of gas, it seems also to bring in its train the formation of large quantities of naphthalene." It is certain, however, that other factors, such as the size, shape, and inclination of the retort with relation to the volume of the charge of coal, and the varying conditions to which the evolved gases are subjected before and during their passage from the retort, have a great deal to do with the quantity of naphthalene formed.

Tars used as road binders are for the most part soft pitches obtained by distilling from 15 to 30 per cent. of the lighter products from the crude material. The soft pitch contains a large proportion of the naphthalene which may have been present in the original tar, and it is the study of the effect of naphthalene upon this grade of material that is the subject of this paper. As consistency is one of the most important properties of a road tar, it was thought well first to investigate the effect of varying percentages of naphthalene upon a given tar.

From its very nature naphthalene itself can be considered as a binding material. For some time past it has been known, however, to serve as a flux

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[1] Published by permission of Director. Office of Public Roads, U. S. Department of Agriculture.

[1] *J. Gas Light.*, **110**, 498 (1910).

for the binding constituents of tars, in spite of the fact that it is a crystalline solid. Thus it is possible to combine, by heating together, a hard tar pitch and a quantity of naphthalene with the formation of a soft product. It was thought, therefore, that a comparison of its fluxing value with that of certain less volatile tar distillates would prove most instructive. For this purpose a representative coal tar was taken and distilled to 238° C. in order to remove all the naphthalene. This naphthalene-free tar pitch, which was used for the following tests, was so hard that it was difficult to make an impression on it with the finger. An arbitrary measure of the consistency of this pitch was then obtained by means of the New York Testing Laboratory float-test apparatus, which is customarily used for this purpose in the routine examination of tar products in the Office of Public Roads.[1]

The float apparatus, briefly described, consists of an aluminum float or cup, 3$^1/_2$ inches in diameter, into which is screwed a small brass conical collar or mold. This collar is $^7/_8$ inch high, with an internal diameter at the top of $^3/_8$ inch and at the bottom of $^1/_2$ inch.

In making the test the brass collar is placed with the small end down on a brass plate which has been previously amalgamated with mercury by first rubbing it with a dilute solution of mercuric chlorid nitrate and then with mercury. A small quantity of the material to be tested is heated in a metal spoon until quite fluid, with care that it suffers no appreciable loss by volatilization and that it is kept free from air bubbles. It is then poured into the collar in a thin stream until slightly more than level with the top. The surplus may be removed after the material has cooled to room temperature, by means of a spatula blade which has been slightly heated. The collar and plate are then placed in a tin cup containing ice water maintained at 5° C. and left in this bath for at least 15 minutes. Meanwhile another cup is filled about three-fourths full of water, placed on a tripod, and the water heated to any temperature at which it is desired to make the test. This temperature is accurately maintained, and is at no time throughout the entire test allowed to vary more than one-half a degree centigrade from the temperature selected. After the material to be tested has been kept in the ice water for at least 15 minutes, the collar and contents are removed from the plate and screwed into the aluminum float, which is then immediately floated in the warmed bath. As the plug of bituminous material becomes warm and fluid it is gradually forced upward and out of the collar until water gains entrance to the float and causes it to sink.

The time in seconds between placing the apparatus on the water and when the water breaks through the bitumen is determined by means of a stop-watch and is taken as a measure of the consistency of the material under examination. Results so expressed are only relative, but they are comparable to within a good degree of precision. The temperature at which the water bath is maintained is purely an arbitrary matter and, for routine work in the office, 32° C. and 50° C. have been selected as a matter of convenience when testing the comparatively soft and comparatively hard road tars.

For the work described in this circular 55° C. and 80° C. were adopted as most convenient temperatures. The former was selected after making a series of float tests upon the prepared coal tar pitch at temperatures varying from 40° C. to 60° C. In these tests it was found that at 40° C. and 45° C. the tar had not softened sufficiently to complete the test at the end of 1 hour; at 50° C. a test of 24 minutes and 18 seconds was obtained; at 55° C., 9 minutes and 47 seconds; and at 60° C., 3 minutes and 45 seconds. The duration of the test at 55° C. seemed most satisfactory as allowing sufficient leeway for comparative results without consuming too much time. It was decided to select 80° C. as a second working temperature, as it was the nearest convenient one to the melting point of naphthalene. It was thought that, by making consistency tests upon the naphthalene tar-pitch mixtures, later described, at both 55° C. and 80° C., the results would show not only how much the mixture softened at the higher temperature, but what differences, if any, might be due to naphthalene below and above its melting point.

When the matter of temperatures had been decided upon and the consistency of the pitch had been determined at these temperatures, naphthalene mixtures were made as follows: Approximately 30-gram samples were accurately weighed into a series of small tin dishes, and varying percentages of c. p. flake naphthalene were added, starting with 0.5 per cent. of naphthalene and gradually increasing this amount to the extent of 30 per cent. In all, 13 samples were prepared. Before adding the naphthalene, each weighed sample of tar was warmed in the tin dish until fairly fluid, after which the naphthalene was added and the mixture well stirred. It was found better to add the naphthalene a little at a time during the process of mixing rather than to add the entire amount at one time, as by so doing there was less danger of losing some of the naphthalene by volatilization and a uniform mixture was more readily obtained. As the naphthalene was added, an increase in the fluidity of the mixtures was readily seen. Where 20 per cent. of naphthalene was used, the mixture was found to be fluid at normal temperatures, whereas the original pitch was semisolid. The naphthalene combined with the tar with surprising readiness and, upon cooling, no traces of the naphthalene could be seen in the resulting mixture, except where high percentages were added. It was found, however, that between 15 and 20 per cent. of naphthalene caused the tar to become saturated. The 15 per cent. mixture was homogeneous when cold, but in the 20 per cent. mixture a small amount of naphthalene crystals separated out upon cooling. This fact indicates that the tar pitch forms a sort of eutectic with naphthalene similar to certain metallic alloys. Above the approximate eutectic of 20 per cent. the

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[1] *Bull.* **38**, 14–16, U. S. Dept. of Agriculture, Office of Public Roads.

naphthalene crystallized out more and more as the percentage was increased. A mixture of 30 per cent. of naphthalene solidified. This was due to the crystallization of the excess of naphthalene. The consistency of this mixture at 55° C. was found to be higher than the preceding mixtures, owing to the separation of the naphthalene, which does not melt at this temperature. At 80° C. the consistency of this mixture was *nil*; that is, it became very fluid, as would naturally be expected. The maximum increase of fluidity of the tar was obtained with 20 per cent. of naphthalene, which is practically the eutectic point. These facts will be noticed on the curves A and A′ (Fig. 1), which show the consistency of the mixtures plotted against the varying percentage of naphthalene.

Curve A shows the decided effect which naphthalene has upon the tar at 55° C., and A′ the effect at 80° C. As the temperature of the water bath during the float test is raised, the curve A will approach A′ and a series of curves might be obtained, lying between A and A′, for water-bath temperatures between 55° C. and 80° C.

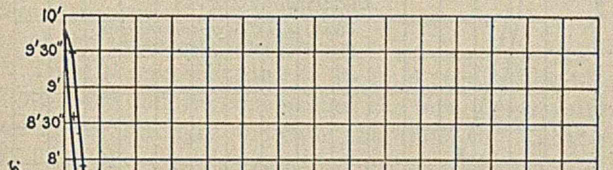

Fig. 1.

The sensitiveness of the tar pitch to small increments of naphthalene is shown by the sharp drop in the first section of curve A, starting with the addition of 0.5 per cent. of naphthalene, which increases the fluidity 1 minute and 12 seconds. The fluidity increases very markedly until 7 per cent. of naphthalene is reached, when the curve becomes more gradual, while increasing percentages of naphthalene have a much smaller effect. The curve drops, however, until 20 per cent. of naphthalene is reached and then rises gradually to 25 per cent. of naphthalene, owing to the separation of naphthalene, as previously explained. At 30 per cent. of naphthalene a sharp rise is noted and the curve, if continued further, would rise almost perpendicularly, because the naphthalene is so much in excess that an accurate measurement of the consistency would be impossible. For reference to the percentage increase in fluidity, owing to increasing increments of naphthalene, the data given in Table I calculated from the curves will show statistically what the curves represent graphically.

Table I.—Percentage Increase in Fluidity of Coal-Tar Pitch, Owing to Additions of Naphthalene and Naphthalene-Free Tar Distillate.

Per cent. of naphthalene or distillate.	Due to naphthalene. At 55° C. Per cent.	Due to naphthalene. At 80° C. Per cent.	Due to distillate. At 55° C. Per cent.	Due to distillate. At 80° C. Per cent.
0.5	12.2	6.7	3.1	3.8
1.0	26.9	11.5	19.1	5.8
1.5	44.5	19.2	29.6	14.4
2.0	50.8	27.9	37.1	17.3
2.5	59.3	32.7	44.6	20.2
3.0	64.1	36.5	49.9	25.0
5.0	76.5	51.0	64.2	39.4
7.0	83.3	63.5	75.1	49.0
10.0	91.5	75.0	82.3	61.5
15.0	94.4	83.7	89.6	74.0
20.0	97.3	90.4	94.5	83.7
25.0	96.9	89.4	96.6	89.4
30.0	88.1	75.0	100.0	100.0

It will be observed that 7 per cent. of naphthalene increases the fluidity of the tar 83.3 per cent. at 55° C., while 20 per cent. increases it 97.3 per cent., showing that the additional 13 per cent. of naphthalene makes an increase of only 14 per cent. in fluidity. This fact is shown by the gradual slope of the curve A between these points as contrasted with the steep slope up to 7 per cent.

For comparison with the consistency results obtained with naphthalene, a portion of the original coal-tar pitch was saved for use in mixtures with a naphthalene-free tar distillate. Duplicate tests were carried out in the same way as were the naphthalene tests, except that equivalent percentages of a naphthalene-free distillate were employed. This distillate was a mixture of oils taken from the distillation of several water-gas tars and showed the following composition upon fractional distillation in an Engler flask:

Table II.—Fractional Distillation of Tar Distillate.

Temperature in ° C.	Per cent. distilled.	Temperature in ° C.	Per cent. distilled.
Up to 190	0.7	Up to 280	47.5
Up to 200	1.0	Up to 290	55.5
Up to 210	1.8	Up to 300	62.5
Up to 220	5.0	Up to 310	71.0
Up to 230	7.5	Up to 320	77.5
Up to 240	14.5	Up to 330	83.0
Up to 250	23.0	Up to 340	89.0
Up to 260	28.5	Up to 346[1]	94.0
Up to 270	37.0		

The specific gravity of this distillate was 1.006 at 25° C. and, upon cooling to —10° C., no solids crystallized out of solution.

Thirteen samples were weighed out in the same manner as for the naphthalene tests and the percentages of distillate added as before. Consistency

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[1] Dry.

results were obtained upon the mixture of tar and distillate, according to the float apparatus, and at the same temperatures as in the naphthalene tests—55° C. and 88° C. The procedure was exactly duplicated in both cases, so that the results could be studied under exactly the same conditions. In Fig. 1 the results of this second series of tests are shown by curves B and B′, and the corresponding tabulated data are shown in Table I as compared with the results from naphthalene.

The effect exerted by naphthalene upon the fluidity of tar is, from these results, a very important one in coal tars used for road construction. All coal tars contain naphthalene, but the amount in road-tar preparations varies from 0 to 10 per cent. and higher. The degree of fluidity which a tar maintains under service conditions is a most important consideration. The fact that a tar is originally of proper consistency for certain work is no reason for supposing that this consistency will be maintained under service conditions. If the fluidity of the tar is due principally to nonvolatile tar oils, it will undoubtedly maintain its original consistency for a longer period than if the fluidity is due mainly to high naphthalene content. Therefore, in two tars of the same consistency or degree of fluidity, one with a small naphthalene content and the other with a high naphthalene content, it would be natural to predict from the foregoing data that upon exposure the low naphthalene tar would maintain its original consistency for a longer time, if other things were equal. Owing to the volatility of naphthalene, the high naphthalene tar would undoubtedly lose more or less naphthalene, and hence its fluidity might be expected to decrease rapidly. This subject is now under investigation and will be covered in a later paper.

In addition to refined coal tars, refined water-gas tars and also refined mixtures of coal tar and water-gas tar are used to a considerable extent in the treatment and construction of roads. For this reason it was thought advisable to determine what effect naphthalene might have upon the consistency of water-gas tar pitch. Water-gas tar as produced in the modern manufacture of carburetted water gas is similar in many ways to its sister product, coal tar. It has, however, marked characteristics in which it differs from coal tar, namely, a lower specific gravity, a lower free-carbon content, and a relatively small amount of naphthalene.

A representative sample of water-gas tar was distilled until the residual pitch had as nearly as possible the same consistency at 55° C. as the coal tar pitch in the previous experiments. This water-tar pitch had a consistency of 9 minutes and 49 seconds. It was divided into two portions, one for naphthalene mixtures and one for distillate mixtures. As in the previous work, samples were weighed out with varying percentages of naphthalene and a duplicate set of samples with an equivalent amount of the same naphthalene-free tar distillate as used in the coal-tar tests. The consistency was obtained in both sets of tests with the float apparatus, and the water bath was maintained at 55° C. and 80° C., respectively. The results from the naphthalene series are shown in Fig. 2 by curves C and C′, and those of the corresponding distillate series by curves D and D′.

It will be noted that these curves follow very closely those shown in Fig. 1 and are of the same general type. The relation between the consistencies obtained with naphthalene and the naphthalene-free distillate is practically the same as for coal tar, and the respective influence of the increase in fluidity is similar, as shown in Table III. Indeed, this similarity is remarkably close when it is realized that the coal-tar pitch contained 18.34 per cent. of free carbon, while the water-gas tar pitch contained only 1.77 per cent. of free carbon.

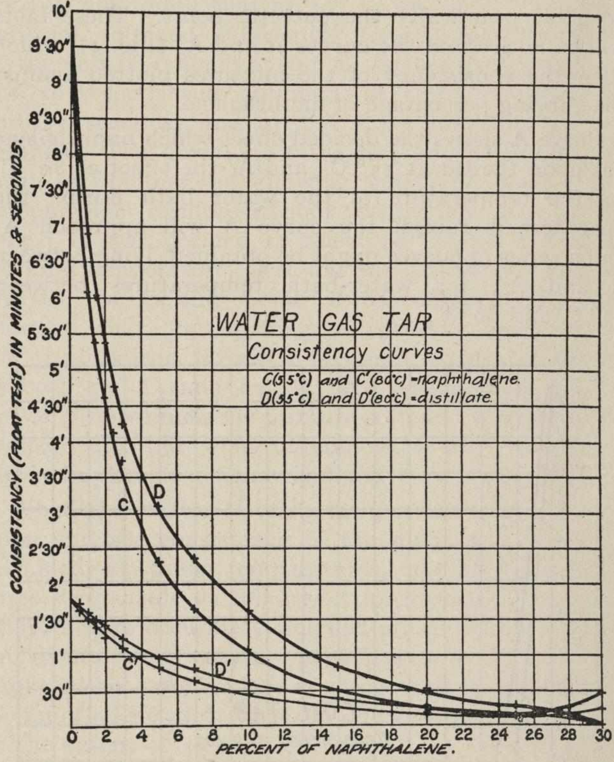

Fig. 2.

TABLE III.—PERCENTAGE OF INCREASE IN FLUIDITY OF WATER-GAS TAR PITCH, OWING TO ADDITIONS OF NAPHTHALENE AND NAPHTHALENE-FREE TAR DISTILLATE.

Per cent. of naphthalene or distillate.	Due to naphthalene.		Due to distillate.	
	At 55° C. Per cent.	At 80° C. Per cent.	At 55° C. Per cent.	At 80° C. Per cent.
0.5	21.1	5.5	18.8	4.6
1.0	38.0	15.6	29.7	11.9
1.5	45.2	22.0	38.5	16.5
2.0	53.0	30.3	45.2	21.1
2.5	57.9	33.0	51.4	26.6
3.0	62.0	38.5	56.7	31.2
5.0	76.4	54.1	68.4	46.8
7.0	83.1	64.2	75.9	55.0
10.0	89.0	75.2	83.5	67.0
15.0	94.9	86.2	91.5	78.9
20.0	97.1	89.9	94.7	86.2
25.0	98.5	92.7	97.1	90.8
30.0	95.2	87.2	100.0	100.0

Comparing these data with those tabulated for the coal-tar tests, it will be noted that the effect of small percentages of naphthalene is even greater for the water-gas tar than for the coal tar of like consistency, and this is also true of the naphthalene-free distillate, although the effect is not so marked. The principal difference between the two sets of curves at 55° C. is the marked increase in fluidity caused by both naphthalene and distillate when only 0.5 per cent. is added, as even as small an addition as this increases the fluidity by 21.1 and 18.8 per cent., respectively. This fact is shown by the sharp drop in both water-gas tar curves at 55° C. The two series of curves obtained at 80° C. are also similar. The effect of increasing amounts of naphthalene, however, is not so markedly shown as in the curves for the test at 55° C.

In a paper by one of the authors,[1] "On the Effect of Free Carbon in Tars from the Standpoint of Road Treatment" it is shown that an increase in the percentage of free carbon to tar bitumen of a given consistency decreases the fluidity of the resulting product. It is evident, therefore, that the true bitumen of the two tar pitches under investigation, excluding free carbon differed somewhat, although the pitches as prepared were of the same consistency.

While at the present time it does not seem advisable to draw very definite conclusions, the foregoing results nevertheless strongly indicate the following facts:

1. That the fluxing value of naphthalene for tar pitches is somewhat greater, although quite similar, to the heavier naphthalene-free tar distillates, until the mixture becomes saturated with naphthalene.
2. That for the harder tar pitches the addition of very small percentages of naphthalene will produce a marked increase in fluidity of the resulting product.
3. That for the softer pitches the addition of naphthalene in small quantities causes less increase in fluidity than for the harder pitches.
4. That where naphthalene is added beyond the point of saturation a rapid decrease in the fluidity of tars at temperatures below the melting point of naphthalene is observed, but at temperatures above its melting point the fluidity continues to increase.

In conclusion, it may be stated that evidence points to the fact that, within a reasonable degree of accuracy, it should be possible to foretell, by reference to the curves which have been given, what consistency to expect from the addition of a given percentage of naphthalene to a tar pitch or refined tar of known consistency, irrespective of the free carbon content of the tar.

OFFICE OF PUBLIC ROADS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON.

A NEW METHOD FOR DETERMINING THE MELTING POINT OF PITCH.

By H. F. FRENCH.

Received September 25, 1911.

As a criterion for the suitability of coal tar pitch for various industrial purposes, the melting-point determination has found considerable application. From the nature of the material, such a point is necessarily arbitrary, being fixed only by the conditions imposed in the method selected.

The methods in general use are rendered rather unsatisfactory, by large personal factors, and essential conditions which are very hard to reproduce exactly. This paper describes a new method, designed to remedy these difficulties.

It consists in heating a suspension of the pulverized material in a solution, under definite conditions, until it coagulates. The temperature at which this coagulation occurs is taken as the melting point. The bath is a very dilute solution of sulphuric acid, heated electrically, in itself furnishing the necessary resistance. The electrolyte is rotated in an Erlenmeyer flask. The remainder of the apparatus proper is a unit, consisting of the electrodes and thermometer.

APPARATUS.

Electrodes are $^3/_{16}$-inch copper rod, rubber-covered and lead-tipped, assembled with a 110° Centigrade thermometer, as shown in the figure.

Flask.—An 8-ounce medium mouth Erlenmeyer flask.

Ammeter.—A direct current instrument with at least a 3 ampere scale, graduated in 0.1 ampere divisions.

Electrical Circuit.—A 220-volt direct current circuit.

Electrolyte.—A dilute solution of sulphuric acid.

Preparation: A stock solution is made up containing 20 cc. of concentrated H_2SO_4, sp. gr. 1.84, per liter. Twenty-five to thirty cc. of this solution are diluted to 1 liter and standardized.

Standardization.—The electrodes are connected to the power circuit, through the ammeter, and a double pole, single throw, knife switch. Fifty cc. of the electrolyte, at about 20° Centigrade, are placed in the flask, and the electrodes introduced. The electrodes should be parallel to one side of the flask with their tips resting upon the bottom. By a few short applications of the current, while rotating the flask, the temperature of the bath is brought to 24° C. At this point the amperage is quickly read. The electrolyte must be of such strength that this reading, which will be obtained at very nearly 25° C., is 2.2 amperes.

Preparation of Material.—About 20 grams of pitch are placed in a one-quart iron mortar, and ground until the bulk of it passes through a screen conforming to the following specifications:

SCREEN SPECIFICATIONS.

Meshes per linear inch.	Number of wire.	Diameter of wire in inches.	Size of openings in inches.
40	32	0.01125	0.0137

The wire number is given according to the Old English Standard Gauge. The screen is made of plain double crimped brass wire cloth.

Determination.—Two grams of the freshly ground material (samples should not be allowed to stand more than one hour after grinding, and should be

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[1] *Proc. Am. Soc. Test. Mat.*, **9**, 549 (1909).

protected from high temperature) are weighed out within 0.1 of a gram. This sample is transferred to the clean flask, which should be rinsed out with distilled water, and the outside wiped dry.

Fifty cc. of the electrolyte at 20–25° C. are then added, the flask closed with a rubber stopper, and the contents mixed by a slight shaking. The electrodes are now introduced and the flask contents rotated in the same manner as in the standardization, the current is switched on for a moment, and the ammeter reading noted.

A variation of more than one-tenth or two-tenths of anampere from the initial reading of the electrolyte alone indicates the introduction of some impurity. Such a determination should be started over. If the condition persists, the impurity is probably being introduced in the sample, and should be investigated. If, however, the amperage is very nearly normal, as will be the case with the vast majority of samples, the determination is continued as follows: The flask contents are rotated in the same manner as before, holding the flask at the level of the eyes, and viewing the contents against a good light. The current is now allowed to pass until the pitch coagulates, when the current is immediately switched off, and the temperature quickly read.

It is important to keep the pitch and electrolyte rotating in one direction throughout the determination, and to continue this rotation until the temperature reading has been obtained. It is also essential to the proper performance of the method that the rapidity of this rotation be kept at a maximum.

In noting the end point, a slight, gradual clearing up of the lower part of the solution must be disregarded, and the treatment continued until the large bulk of the material rapidly coagulates into a "gob." Each figure reported should be the average of several determinations.

RANGE AND ACCURACY.

The range of the method is limited by the fact that the samples must be ground as specified, and by the boiling point of the electrolyte. It will be found that these limits allow of the application of the method to practically all samples of what is commonly known as hard pitch. Some experimental work has been done along the line of applying this method to softer varieties of material, by grinding at very low temperatures. These applications, however, have not been worked up extensively, and are, at best, rather inconvenient.

The accuracy of the method is shown by Table 1, which includes all the results obtained during the recent investigation of some special samples. It will be noted that the average figures, obtained by two analysts, who worked independently, agree easily within 1° Centigrade. In addition, this data demonstrates the effect of allowing samples to stand in the ground condition, a point which will receive further mention.

Samples had stood for 15 days in pasteboard containers, after being ground, before the determinations were made.

Variety of pitch.	Sample number.	Analyst A.		Analyst B.				Difference between av. A and B.
		Det. No. 1.	Det. No. 2.	Det. No. 1.	Det. No. 2.	Av. A.	Av. B.	
1	1	70.5	70.5	71.0	71.0	70.5	71.0	0.5
2	2	75.0	75.0	75.5	75.0	75.0	75.2	0.2
3	3	83.0	82.0	82.5	83.0	82.5	82.7	0.2
Freshly ground samples of the same varieties of pitch.								
1	4	65.0	66.0	65.5	..	65.5	65.5	0.0
2	5	71.5	72.0	71.5	..	71.7	71.5	0.2
3	6	82.0	82.0	82.5	..	82.0	82.5	0.5
Same samples (4, 5 and 6) after having stood 10 days in pasteboard containers since being ground.								
1	7	70.5	71.5	71.0	71.5	71.0	71.2	0.2
2	8	75.0	75.5	75.0	75.5	75.2	75.2	0.0
3	9	82.5	83.0	83.5	84.0	82.7	83.7	1.0
Same samples (7, 8 and 9) after having stood in the same conditions for 3 additional days near hot steam pipes.								
1	10	73.0	73.0	72.5	..	73.0	72.5	0.5
2	11	76.0	77.0	77.5	..	76.5	77.5	1.0
3	12	84.0	83.0	83.5	..	83.5	83.5	0.0
Miscellaneous samples.								
		65.0	65.0	66.0	65.5	65.0	65.7	0.7
		71.5	71.0	72.0	71.5	71.2	71.7	0.5
		72.0	72.0	71.5	71.0	72.0	71.2	0.8
		74.0	74.5	74.0	..	74.2	74.0	0.2
		78.0	77.5	77.0	77.0	77.7	77.0	0.7
		79.5	79.5	80.0	..	79.5	80.0	0.5
		82.0	82.0	82.5	82.5	82.0	82.5	0.5
		86.0	85.5	85.5	86.5	85.7	86.0	0.3
		86.5	86.0	86.5	..	86.2	86.5	0.3

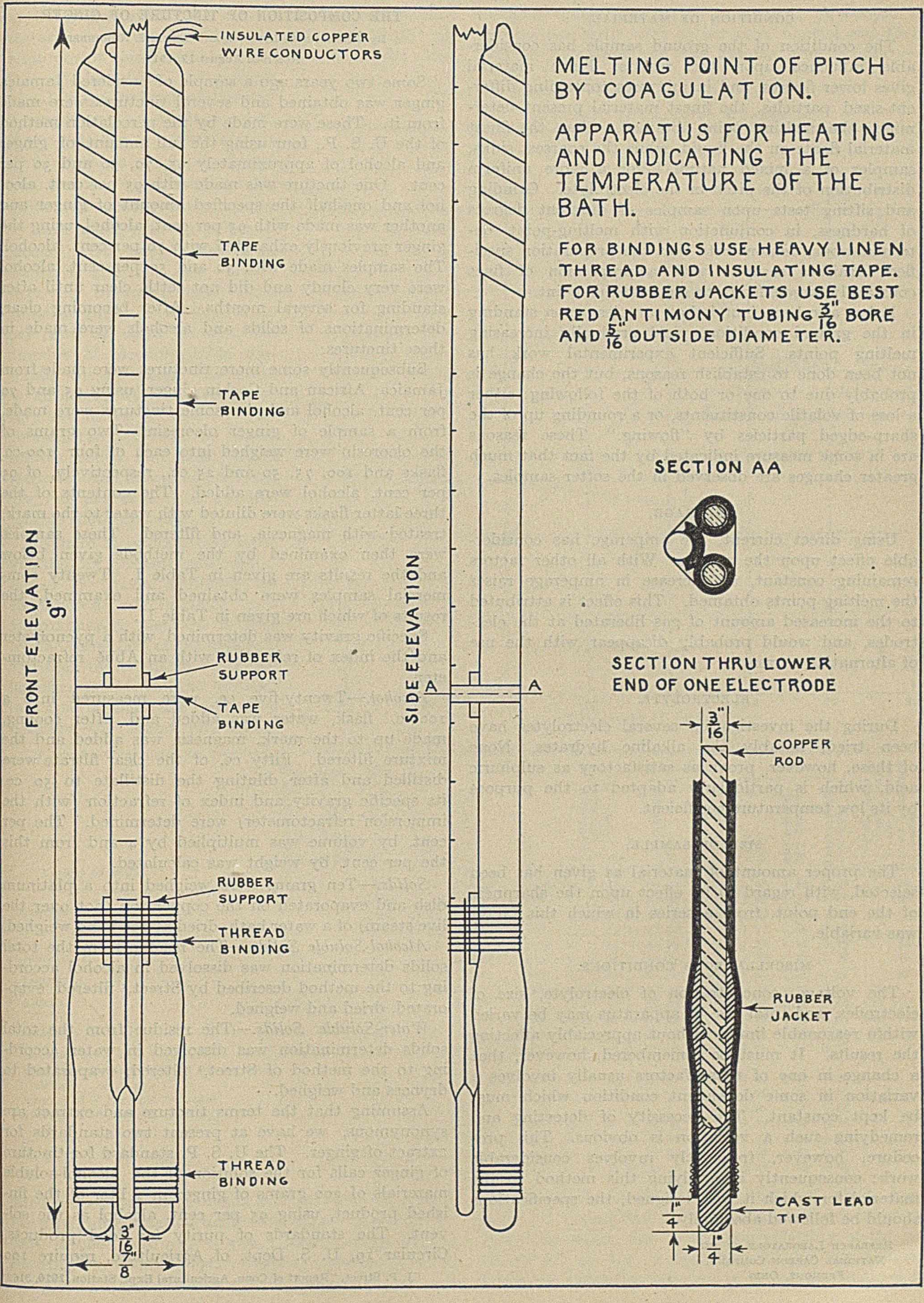
A brief discussion of some additional points may be of interest to any who desire a modification applicable to other materials, and serve to indicate the necessity of the conditions imposed.

HEATING RATE.

Results during the preliminary work led to the conclusion that the heating rate had considerable effect upon the figures obtained. Upon this basis the electrical method of heating was developed, and for some time it was thought necessary to standardize the electrolyte by the rise in temperature over a definite time period of current flow. Subsequent work, however, has disqualified the findings of the earlier experiments, and has shown that the heating rate may be varied considerably without affecting the results to any appreciable extent. Since other methods of heating have not proved nearly so satisfactory as the electrical, this feature has been retained, and the standardization obtained in terms of the amperage, a condition, which, as mentioned below, has considerable effect upon the results.

SHAPE AND SIZE OF APPARATUS.

The apparatus specified has been developed through several more complicated forms. The essential advantage of the one adopted lies in the fact that the rapid rotation throws the bulk of the liquid to the circumference of the flask bottom, thus allowing the electrode tips and thermometer bulb to come into contact with the maximum amount of electrolyte in a given time. This favors a uniform and rapid heat distribution, and a prompt indication of temperature. The same fact permits of the use of a minimum depth of solution, which aids materially toward a rapid end point.



MELTING POINT OF PITCH BY COAGULATION.

APPARATUS FOR HEATING AND INDICATING THE TEMPERATURE OF THE BATH.

FOR BINDINGS USE HEAVY LINEN THREAD AND INSULATING TAPE. FOR RUBBER JACKETS USE BEST RED ANTIMONY TUBING $\frac{3}{16}''$ BORE AND $\frac{5}{16}''$ OUTSIDE DIAMETER.

CONDITION OF MATERIAL.

The condition of the ground sample has considerable influence upon the results. Finer material gives lower figures, and in mixtures containing different-sized particles, the finest material present determines the melting point obtained. Since the finest material floats on the liquid, while the coarsest sinks, samples of a mixed nature favor a more uniform distribution of the pitch in the electrolyte. Grinding and sifting tests upon samples of different degrees of hardness, in conjunction with melting-point determinations, demonstrate that the preparation specified furnishes samples with a proportion of fines constantly large enough to regulate this point.

It has also been found that samples, upon standing in the ground condition, yield gradually increasing melting points. Sufficient experimental work has not been done to establish reasons, but the change is probably due to one or both of the following: either a loss of volatile constituents, or a rounding up of the sharp-edged particles by "flowing." These reasons are in some measure indicated by the fact that much greater changes are observed in the softer samples.

AMPERAGE.

Using direct current, the amperage has considerable effect upon the results. With all other factors remaining constant, an increase in amperage raises the melting points obtained. This effect is attributed to the increased amount of gas liberated at the electrodes, and would probably disappear with the use of alternating current.

ELECTROLYTE.

During the investigation several electrolytes have been tried, notably the alkaline hydrates. None of these, however, prove as satisfactory as sulphuric acid, which is particularly adapted to the purpose by its low temperature coefficient.

SIZE OF SAMPLE.

The proper amount of material as given has been selected, with regard to its effect upon the sharpness of the end point, from a series in which this factor was variable.

MISCELLANEOUS CONDITIONS.

The voltage, concentration of electrolyte, size of electrodes, and total size of apparatus may be varied within reasonable limits without appreciably affecting the results. It must be remembered, however, that a change in one of these factors usually involves a variation in some dependent condition which must be kept constant. The necessity of detecting and remedying such a variation is obvious. This procedure, however, frequently involves considerable work; consequently in applying this method to the material for which it was designed, the specifications should be followed absolutely.

RESEARCH LABORATORY OF THE
NATIONAL CARBON COMPANY,
FREMONT, OHIO.

THE COMPOSITION OF TINCTURE OF GINGER.

By HERMANN C. LYTHGOE AND LEWIS I. NURENBERG.

Received August 12, 1911.

Some two years ago a sample of powdered Jamaica ginger was obtained and several tinctures were made from it. These were made by the percolation method of the U. S. P., four using the full amount of ginger and alcohol of approximately 95, 70, 50 and 30 per cent. One tincture was made with 95 per cent. alcohol and one-half the specified amount of ginger and another was made with 95 per cent. alcohol, using the ginger previously exhausted with 70 per cent. alcohol. The samples made with 30 and 50 per cent. alcohol were very cloudy and did not settle clear until after standing for several months. After becoming clear, determinations of solids and alcohols were made in these tinctures.

Subsequently some more tinctures were made from Jamaica, African and Cochin ginger, using 95 and 70 per cent. alcohol and also some tinctures were made, from a sample of ginger oleoresin. Two grams of the oleoresin were weighed into each of four 100-cc. flasks and 100, 75, 50 and 25 cc., respectively, of 95 per cent. alcohol were added. The contents of the three latter flasks were diluted with water to the mark, treated with magnesia, and filtered. These samples were then examined by the methods given below and the results are given in Table I. Twenty commercial samples were obtained and examined, the results of which are given in Table II.

Specific gravity was determined with a pycnometer and the index of refraction with an Abbé refractometer.

Alcohol.—Twenty-five cc. were measured into a 100-cc. flask, water was added and, after cooling, made up to the mark, magnesia was added and the mixture filtered. Fifty cc. of the clear filtrate were distilled and after diluting the distillate to 50 cc. its specific gravity and index of refraction (with the immersion refractometer) were determined. The per cent. by volume was multiplied by 4 and from this the per cent. by weight was calculated.

Solids.—Ten grams were weighed into a platinum dish and evaporated on the copper top (not over the live steam) of a water bath, dried at 100° and weighed.

Alcohol-Soluble Solids.—The residue from the total solids determination was dissolved in alcohol according to the method described by Street,[1] filtered, evaporated, dried and weighed.

Water-Soluble Solids.—The residue from the total solids determination was dissolved in water according to the method of Street,[1] filtered, evaporated to dryness and weighed.

Assuming that the terms tincture and extract are synonymous, we have at present two standards for extract of ginger. The U. S. P. standard for tincture of ginger calls for the solution of the alcohol-soluble materials of 200 grams of ginger in 1 liter of the finished product, using 95 per cent. alcohol as the solvent. The standards of purity for food products, Circular 19, U. S. Dept. of Agriculture, require 100

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[1] J. P. Street, "Report of Conn. Agricultural Expt. Station, **1910**, 516."

cc. of ginger extract to contain the alcohol-soluble material from not less than 20 grams of ginger, no requirement being made as to the strength of the alcohol. It has been the custom to call ginger extract adulterated if made with weak alcohol. Street has shown[1] that extracts made from 60 per cent. alcohol are weaker in alcohol-soluble solids and consequently inferior to those made with 95 per cent. alcohol. Our work, as given in Table I and the plot, shows that in tinctures made from Jamaica ginger if alcohol of 70 per cent. or more is used, the amount of alcohol-soluble material will be about the same in all cases. As the strength of the extracting alcohol is decreased the per cent. of water-soluble solids and total solids increase, and using alcohol below 70 per cent. the alcohol-soluble solids decrease.

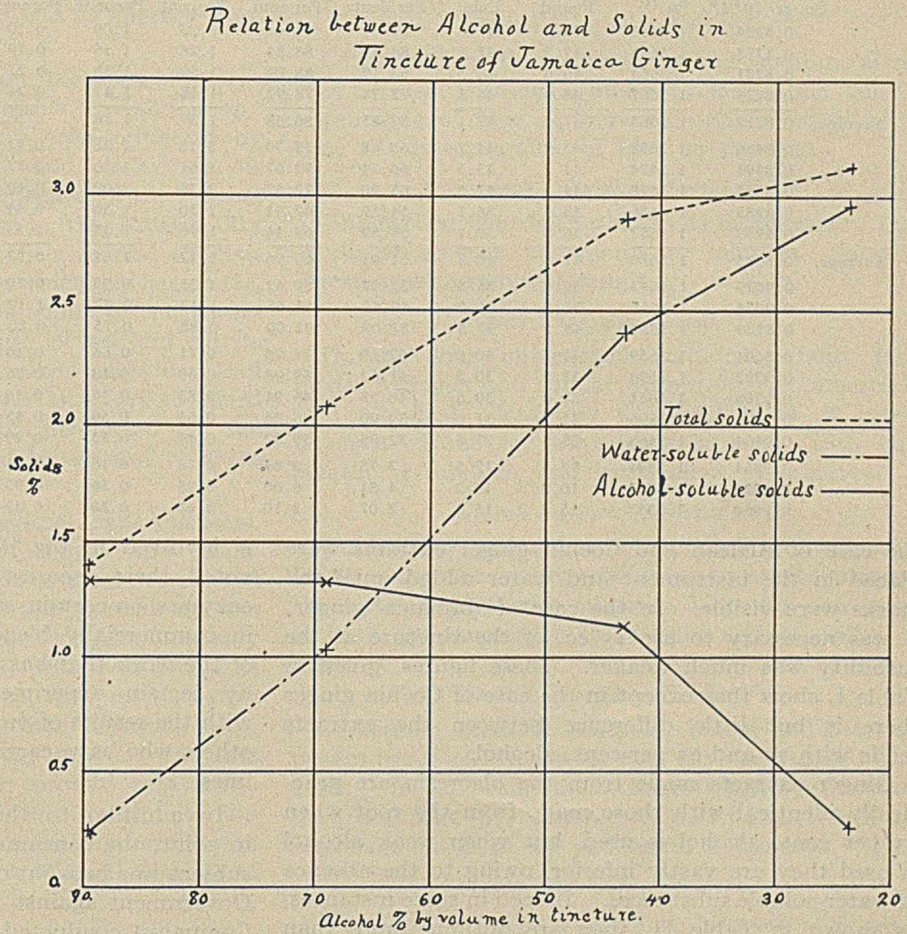

TABLE I.—COMPOSITION OF TINCTURE OF GINGER MADE FROM DIFFERENT VARIETIES OF GINGER AND VARYING STRENGTHS OF ALCOHOL.

Variety of ginger.	Alcohol extract of ginger. Per cent.	Cold water extract of ginger. Per cent.	Ginger used per liter. Grams.	Alcohol used. Per cent.	Sp. gr., 20°/4°.	n_D 20°.	Refraction of alcoholic distillate. 20°. Found.	Calc.	Alcohol. By weight. Per cent.	By volume. Per cent.	Solids. Total. Per cent.	Alcohol-soluble. Per cent.	Water-soluble. Per cent.	Water used in Feser lactoscope. Amt. of tincture used. 10 cc.	15 cc.
Jamaica	5.90	17.30	200	94.53	0.8184	1.3662	47.8	47.5	85.38	89.76	1.40	1.33	0.24	...	60
			200	73.30	0.8863	1.3664	39.2	38.7	61.46	69.08	2.08	1.33	1.04	...	60
			200	49.29	0.9462	1.3609	29.6	29.5	36.66	43.68	2.89	1.13	2.40	...	..
			200	29.58	0.9794	1.3518	22.1	22.1	19.13	23.44	3.11	0.30	2.96	...	..
Jamaica	4.85	17.10	200	95.40	0.8174	1.3658	47.1	46.9	84.70	89.24	1.38	1.10	0.19	...	50
			200	69.34	0.8933	1.3662	37.2	36.9	56.36	64.16	2.22	1.45	1.14	...	70
Jamaica	....	...	200	95.0	0.8189	1.3657	47.3	46.7	84.19	88.84	1.60	1.24	0.22	...	40
African	6.40	12.55	200	95.40	0.8173	1.3665	47.5	46.9	84.84	89.36	1.86	1.84	0.08	105	..
			200	69.34	0.8881	1.3660	37.9	37.7	59.35	66.08	1.90	1.34	0.44	120	..
Cochin	6.95	17.00	200	95.40	0.8181	1.3666	47.5	46.9	84.70	89.24	2.19	1.94	0.22	140	..
			200	69.34	0.8889	1.3672	37.0	36.8	55.73	63.56	3.08	1.47	1.86	80	..
Jamaica	5.90	17.30	100	94.53	0.8156	1.3645	48.1	47.9	87.82	91.64	0.70	0.67	0.21	...	..
Jamaica exhausted with 73.30 per cent. alcohol	....	...	200	94.53	0.8352	1.3650	46.1	46.1	82.32	87.36	0.18	0.18	0.06	...	..
Average of 95 per cent. tinctures	....	...	200	95.15	0.8180	1.3662	....	....	...	89.29	1.68	1.49	0.19	...	..
Average of 70 per cent. tinctures	....	...	200	69.34	0.8901	1.3665	....	....	...	66.40	2.40	1.15	1.42	...	..
Ginger of oleoresin	....	...	20	95.0	0.8144	1.3668	49.0	47.9	87.24	91.12	1.24	1.16	0.10	...	..
			20	75.0	0.8807	1.3658	40.3	38.9	65.06	72.44	1.05	0.86	0.51	...	..
			20	50.0	0.9389	1.3593	30.5	29.7	38.23	45.40	1.03	0.50	0.79	...	..
			20	25.0	0.9762	1.3484	22.4	21.9	19.33	23.68	0.95	0.18	0.92	...	..

As there is undoubtedly some volatile oil present, not determined by these methods, we endeavored to discover and approximately measure it first by the refraction of the distillate and then by means of the Feser lactoscope. It will be noticed in Table I that the difference between the found and calculated refractions of the alcoholic distillate in the case of Jamaica ginger tincture made from 95, 70, 50 and 30 per cent. alcohol were 0.3, 0.5, 0.1 and 0, respectively, showing less volatile high refracting substances in the tinctures made with the weak alcohol. A sample of the tincture made with 95 per cent. alcohol was then distilled undiluted and the specific gravity and refraction of the distillate taken, both of which were found to correspond to the same strength alcohol. This is no doubt due to the non-volatility of the essential oil at the temperature of boiling alcohol. Using the Feser lactoscope, 10 cc. of the tincture in

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[1] J. P. Street, "Report of Conn. Agricultural Expt. Station, **1910**, 505."

TABLE II.—COMPOSITION OF COMMERCIAL TINCTURES OF GINGER.

			Refraction of alcoholic distillate 20°.		Alcohol.		Solids.			
	Sp. gr. 20°/4°.	n_D 20°.	Found.	Calc.	By weight. Per cent.	By volume. Per cent.	Total. Per cent.	Alcohol-soluble. Per cent.	Water-soluble. Per cent.	Remarks.
	0.8224	1.3660	46.3	47.8	87.81	91.64	1.23	1.09	0.10	U. S. P.
	0.8173	1.3655	47.2	47.8	84.19	88.84	1.26	1.16	0.19	
	0.8221	1.3665	46.6	46.5	83.19	88.04	1.59	1.38	0.27	
	0.8229	1.3667	48.0	46.5	72.28	78.92	1.48	1.47	0.24	
Average,	0.8212	1.3663	47.0	47.1	81.85	86.68	1.39	1.28	0.20	
	0.8436	1.3688	45.9	44.7	68.68	75.70	2.72	2.36	0.71	Good tinctures but not U. S. P. Low in alcohol.
	0.8491	1.3674	44.8	43.5	66.74	73.67	1.61	1.40	0.57	
	0.8555	1.3678	44.3	42.5	65.20	72.57	2.34	2.02	0.49	
	0.8985	1.3656	36.4	36.1	54.59	62.44	2.30	1.30	0.84	
	0.8959	1.3652	36.6	36.1	54.59	62.44	1.90	1.33	1.23	
Average,	0.8685	1.3670	41.6	40.5	61.95	69.96	2.17	1.68	0.77	
	0.9029	1.3642	36.0	35.5	52.58	60.44	1.33	0.95	0.70	Low in alcohol and ginger.
	0.9054	1.3645	36.8	36.0	49.60	54.65	1.42	0.67	1.12	Made from exhausted ginger.
	0.8129	1.3651	48.1	47.5	87.00	91.00	0.88	0.75	0.10	Low in ginger.
	0.8601	1.3659	41.7	40.9	67.60	74.76	0.71	0.66	0.10	Made from oleoresin of ginger and weak alcohol.
	0.9292	1.3596	31.5	30.5	41.62	49.08	0.60	0.18	0.36	
	0.9308	1.3651	31.0	30.5	40.58	46.91	0.73	0.46	0.54	
	0.9321	1.3596	31.7	31.0	39.00	46.25	0.64	0.56	0.45	
	0.9464	1.3563	28.3	27.8	32.93	39.52	0.46	0.33	0.29	
	0.9864	1.3394	17.4	17.5	7.75	9.64	0.73	0.16	0.71	Made from oleoresin of ginger, capsicum and very dilute alcohol.
	0.9931	1.3383	16.2	16.2	4.81	6.00	0.98	0.36	0.96	
	0.9960	1.3357	15.2	15.6	2.07	2.10	0.43	0.28	0.39	

the case of African and Cochin ginger extracts were placed in the instrument and water added until the marks were visible. In the case of Jamaica ginger, it was necessary to use 15 cc. of the tincture as the turbidity was much weaker. These figures, given in Table I, show that except in the case of Cochin ginger there is but little difference between the extracts made with 70 and 95 per cent. alcohol.

Ginger extracts made from the oleoresin are practically identical with those made from the root when 95 per cent. alcohol is used, but when weak alcohol is used they are vastly inferior, owing to the absence of water-soluble substances. Indeed in some instances, as shown in Table II, they are nothing more than alcoholic beverages or colored water.

LABORATORY OF FOOD AND DRUG INSPECTION,
MASS. STATE BOARD OF HEALTH,
BOSTON.

AGING OF FLOUR AND ITS EFFECT ON DIGESTION.[1]

By J. A. WESENER AND GEORGE L. TELLER.

Received March 6, 1911.

A great deal of work has been done on the subject of bleached flour with reference to the so-called nitrite and nitrite-reacting material, and how these substances might affect other constituents of the flour, and the use of the flour as an article of food. In a former paper published by us in THIS JOURNAL,[1] we gave a full bibliography of the work which had been done up to July, 1909, with the exception of one article by Ladd and Bassett,[2] which had not come to our notice, and which appeared in the March issue, 1909, of the *Journal of Biological Chemistry.* Since then other experimenters have written on this subject.

In the many digestion experiments which have been made in the effort to throw some light on the influence of flour bleaching upon digestion, the writers appear to have lost sight of the true chemistry which is involved in the bleaching of flour, and have devoted their energies to investigating the action of enzymes on certain substances which are not present in commercially bleached flour.. Furthermore, much of the work that has been done with these substances by certain experimenters is markedly at variance with the results of our own investigations and of some others who have carried out experiments along similar lines.

In addition to the articles which have appeared in print, the consummation of the work done on this subject was brought out in a suit by the United States Government against the Lexington Mill and Elevator Company[3] conducted at Kansas City in June, 1910.

Ladd[2] failed to call attention to our work previously published on this subject. This could not have been an oversight, for our article appeared in the same number of the *American Food Journal* in which one of his own articles was published, and he has in no other place attempted to refute the arguments which we there presented in direct refutation of numerous essential points in articles published by himself.

Attention should be called to two important errors which appear in Ladd and Bassett's[2] work. On page 76 where they have stated that the nitrogen as nitrite nitrogen in the patent flour which they used was 6.8 parts per million, and in the clear flour 12.95 parts per million, while giving the amount in five grams of the patent flour 0.0034 milligram nitrogen and in the clear flour 2.4159 milligrams of sodium nitrite for 373 grams of the flour. The correct placing of the decimal point would make the amount of nitrite nitrogen in the patent flour 0.68 part per million and in the clear flour 1.29 parts per million of nitrite-reacting nitrogen. These amounts agree closely with what has been conceded to be the average amount of nitrite-reacting nitrogen found in commercially bleached flours. Without entering into detailed criticism, attention should be called to the fact that Ladd has introduced into this article, without new data, conclusions taken from one of his former

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[1] Read at the summer meeting of the American Chemical Society, Indianapolis, June, 1911.

publications, and to which we had replied in detail.[4] For example, references to iodine absorption by the oil of bleached and unbleached flours, and the presence of nitrogen in the oil of bleached and its absence from the oil of unbleached flours.

The digestion experiments on bleached flour as conducted by Ladd and Bassett,[2] Halliburton,[5] Mann,[6] and Hale[7] have already been criticized by Prof. Rockwood.[8] The method used by him in his experiments was one which we outlined at the request of the attorneys for the defense in the Kansas City trial, and which was used by their several experts. In addition to the experiments which he has made, we have increased largely the amount of nitrite-reacting nitrogen both by the use of sodium nitrite and by the use of nitrous and nitric acids in bread and flour, and we have also made an effort to guard against the fallacies and errors introduced by the crude methods which were used by several of these experimenters.

The methods used by the several experimenters, including Ladd,[2] Halliburton,[5] Mann[6] and Hale[7] are open to criticism, in that none of them determined the actual weight of the digested proteid by the nitrogen determination. This we consider the only reliable and absolute method by which to arrive at concordant and positive results. We present below a series of experiments, the purpose of which is to show the actual workings of the different enzymes on the starch, gluten and other proteid substances. The protein digestion was not only determined by ocular measurements, but by actual determination of the nitrogen and the total solids in solution in the digestive fluid.

DIGESTION EXPERIMENTS ON STARCH FROM FLOUR WHICH HAD BEEN BLEACHED WITH NITROGEN OXIDES.

For the purpose of obtaining information as to the reliability of Dr. Halliburton's[5] experiments, in which he claims to have found wide differences in the rate of conversion of starch into sugar by saliva when nitrites in small quantities were present and when they were absent, the following experiments were carried out.

In these experiments were used fresh undiluted saliva, a freshly prepared solution of medicinal pancreatin made by dissolving 0.6 gram of the pancreatin in 100 cc. of water; thin solutions of starch well boiled and diluted with water to make approximately 1.5 grams in 200 cc.; and a solution of sodium nitrite prepared by dissolving 2.1 grams of a good quality of commercial sodium nitrite (more than 99 per cent. pure) in 100 cc. of water. In carrying out the experiments 10 cc. of the starch solution were used, together with 10 cc. of either the saliva or the pancreatin solution and sufficient nitrite solution or its equivalent of water to make a total of 21 cc. These several mixtures were put in a water bath, heated to 40° C. and the digestion allowed to continue until a drop of the liquid brought in contact with a drop of a dilute iodin solution showed no further blue color, this being substantially the experiment carried out by Halliburton. The results of these experiments are detailed below.

Starch Digestion, Series I.

Cornstarch with pancreatin and sodium nitrite 0, 1 to 1000, 1 to 2000, and 1 to 3200, time till disappearance of blue 14 minutes. Same using saliva, time till disappearance of blue 20 minutes.

Starch Digestion, Series II.

Unbleached flour with nitrites as in Series I. Time of digestion with pancreatin 27 minutes. Time of digestion with saliva 16 minutes.

Starch Digestion, Series III.

Durum flour unbleached containing faint trace nitrite nitrogen and similar durum flour commercially well bleached containing a strong trace of nitrite nitrogen. Time for conversion of each: with pancreatin 22 minutes, and with saliva 17 minutes.

Starch Digestion, Series IV.

Unbleached flour and same after exposure to kitchen for ten days, the former containing no nitrite nitrogen, the latter 3 parts per million. Time for conversion of both by pancreatin 33 minutes and by saliva 29 minutes.

Starch Digestion, Series V.

Cornstarch (alkaline reaction) before and after exposure to air of kitchen for two days and three nights during which exposure the nitrite nitrogen was increased from 0.4 part per million to 3.46 parts. Time for conversion of both by pancreatin 8 minutes.

Starch Digestion, Series VI.

Wheat flour unbleached and bleached by Alsop process 3, 6 and 18 times and containing nitrite nitrogen 0, 2, 5 and 15 parts per million. Time for conversion with pancreatin 20 minutes each.

A possible explanation as to why Halliburton, and perhaps others, was misled in his experiments on starch lies in the fact that some slight excess of iodine is necessary in the presence of protein to produce the blue color with starch. The decomposition of the potassium iodide by nitrites increases the iodine present and produces the blue color where it would be otherwise not apparent because of the deficiency of iodine. Careful experiment along this line has clearly shown this to be true, especially where the larger amounts of nitrite were used.

To get information concerning the reliability of the data obtained by Ladd and also by Halliburton on the digestion of gluten by pepsin, the following experiments were carried out:

Before detailing these experiments attention should be called to the great difficulty of experimenting with material of the nature of raw gluten and also to the fact that raw gluten as it is separated out in the laboratory is never used as an article of food, and that we do not, in the actual consumption of flour, meet with any of the conditions which we get in carrying out the experiments with raw gluten as they were carried out by these two authors.

In carrying out the experiments detailed by Ladd, it was thought best to make an additional series of experiments using a tube containing a perforated disk at the bottom which could be made much more uniform than the tubes containing glass wool which he describes. Tubes used for this purpose were those belonging to the Knorr apparatus for the extraction of fat and consisted of glass tubes about ³/₄″ in diameter, 6″ long and with a platinum disk sealed into the tube near the bottom. Tubes were selected in which the perforations in the disks were as nearly uniform as possible. It is hardly to be expected that tubes made in the manner described by Ladd could be uniform, for it would be practically impossible to pack the glass wool so that it should be always the same.

In these experiments as first carried out, ten grams of the flour were washed for gluten and the entire mass of gluten recovered inserted into a tube for each comparative test. The tube was then put in a pepsin digestive fluid prepared substantially as described in the United States Pharmacopeia. The reference given by Ladd to Simon's "Physiological Chemistry" was evidently in error, for in consulting the three editions of this work no description of a solution of this kind was found. He had evidently meant to refer to a book entitled "Manual of Chemistry" by the same author.

The pepsin solution used in these experiments consisted of 500 milligrams of best scale pepsin dissolved in one liter 0.3 per cent. hydrochloric acid solution. Temperature at which the digestion was allowed to take place was practically that of blood heat, being as near 98° F. as possible. A considerable number of these experiments were carried on, all of which led to the same conclusion; namely, that any differences which were apparent in the rate of digestion of the glutens in the several tubes were due to causes other than the presence or absence of nitrites introduced in the flour by the process of bleaching.

The following series may be given as illustrating the results obtained: in this experiment, instead of depending upon the eye to determine when the gluten was sufficiently disintegrated to pass out of the tube, an aliquot part of the liquid was evaporated to dryness and the solids determined. The results given below are the weights in grams of the solids obtained from 10 cc. of liquid withdrawn from each of the bottles in which the digestion was carried on, the same being taken at the end of 21 hours. In this experiment the flour used was the same flour not bleached, bleached 3 times, 6 times, and 18 times by the Alsop process, the amount of nitrite nitrogen being respectively none, 2, 5 and 15 parts per million. The results are given in the following table.

TABLE I.

Showing amount of gluten disintegrated in tubes as used by Ladd:

9189.	Nitrites in parts per million.	Glass wool tubes. Solids in 10 cc. of digestive fluid.	Fat tubes.
Not bleached	None	0.102	0.102
3 times bleached	2	0.097	0.115
6 times bleached	5	0.093	0.096
18 times bleached	15	0.118	0.119
9188.			
Not bleached	0	0.136	0.127
3 times bleached	1.4	0.110	0.106
6 times bleached	3.4	0.091	0.130

In another experiment carried on to show primarily the great source of error in this method of experimenting, the same flour was taken throughout the entire series, and the glutens obtained by washing the ten grams of flour were treated the same throughout except that in one pair it was tightly folded, in another medium tightly folded, and in a third loosely folded. It will be seen from this table that in those tubes which contained glass wool there is a wide variation in the amount of solids obtained, due unquestionably to differences in the tubes, although the tubes were made as nearly uniform as possible. The same wide variation is not apparent in the series using the fat tubes.

TABLE II.

Showing variations in results obtained for gluten from same flour, not bleached, when digested as described by Ladd:

	Glass wool tubes. Solids in 10 cc. of digestive fluid.	Fat tubes.
Tight fold	0.096	0.133
Medium fold	0.057	0.132
Loose fold	0.082	0.134

Another series of experiments on the digestion of the raw gluten was carried out substantially as described by Halliburton. 10 grams of moist gluten obtained from the flour used in the experiment tabulated in Table I were introduced into a flask containing 100 cc. of the same pepsin digestive fluid and allowed to digest over night or for about 16 hours. It will be seen from Table III that the results in this experiment are such as to give the greatest apparent digestion for that bleached 3 and 6 times and least for that bleached 18 times, whereas in Table I the greatest digestion was shown for that bleached 18 times. Here again we have strong proof that the variations are due to cause other than the presence of nitrites.

TABLE III.

Gluten digested as described by Halliburton, using ten grams moist gluten in flask containing pepsin solution:

Figures represent grams. Flour 9189.	Moist gluten.	Total dry gluten taken.	Gluten not disintegrated.	Crude gluten disintegrated as determined by evaporation.	Digested gluten calculated from nitrogen.
Not bleached	10	3.34	1.045	2.071	1.616
3 times bleached	10	3.26	1.011	2.027	1.632
6 times bleached	10	3.48	1.118	2.336	1.942
18 times bleached	10	3.49	1.513	1.90	1.510

Still further proof of the fallacy of the results of Halliburton's and Ladd's experiments on the digestion of gluten is apparent from experiments on bread in which nitrites were absent as compared with other experiments in which they were present in considerable quantities. These experiments may be divided into four series.

In the first series bread from the same unbleached flour was made in the usual manner and also by introducing into the water used in making the dough a quantity of the mixed nitrous and nitric acid produced by the solution of nitrogen oxides in water. In the second series the same bread was treated with pepsin hydrochloric acid liquid with and without the addition of varying quantities of sodium nitrite. In the third series flour was used in place of bread as in experiment 2, while in the fourth series the same bread was used throughout the experiment and the hydrochloric acid was replaced wholly or in part by nitrogen acids produced by dissolving nitrogen oxides in water. In all of these experiments the results agree in showing that unless exceedingly large quantities of nitrites are present there is no retardation of the process of digestion.

BREAD DIGESTION EXPERIMENT NO. 1.

Two loaves of bread were made from Pillsbury's Best flour, not bleached, using 350 grams flour for each. One was made according to our regular formula; the other made in an exactly similar manner, except that in making the dough a part of the water was replaced by sufficient acid, prepared as described below, to equal 10 cc. of decinormal alkali. The acid was prepared by passing into water nitrogen oxides produced by diluting well with air the gases given off by acting on ferrous sulphate by nitric acid. The amount of nitrous acid present in this liquid was determined both by use of potassium permanganate and colorimetrically, and it was found that of the acid present in the 10 cc. of decinormal acid used 7.6 cc. were to be attributed to nitrous acid and 2.4 cc. to nitric acid. The two loaves of bread produced did not differ materially in any particular except that the one containing the acid was a trifle larger and of better form, just as we have often found by adding a small amount of other acids to bread. It is worthy of note that the bread from the loaf containing the acid was not more bleached than the other, showing that the bleaching gases act on the coloring matter of the flour only when the flour is in its dry condition. The acidity of the two loaves of bread was determined and, expressed as lactic acid, was 0.22 per cent for the loaf without the acid, and 0.20 per cent. for the loaf with the acid. The nitrite nitrogen in the bread without acid was 0.03 part per million, and that from the one containing the acid was 0.2 part per million. The nitrite nitrogen added to the loaf containing the acid was 30 parts per million calculated on the flour. The original flour contained traces of nitrites taken up from the air.

On the morning after the bread was baked portions of the interior of each loaf were grated as uniformly as possible. The crust was rejected to permit of greater uniformity of sample. 20 grams of each bread were introduced into a bottle and to each was added 200 cc. of a solution of pepsin and acid, containing 0.100 gram of pepsin and sufficient hydrochloric acid to make 0.3 per cent. To another two bottles were added 20 grams of each bread and 200 cc. of a pancreatin solution containing 0.112 gram pancreatin and 0.6 gram sodium bicarbonate. Also two other bottles containing bread and water only. All were kept at a temperature of 38° C. for one hour after which they were filtered and 25 cc. of each filtrate taken in duplicate for the determination of nitrogen by the Kjeldahl method. The results obtained were as follows, after correcting for the pepsin and pancreatin added and expressed as protein in per cent. of bread taken:

	Plain loaf. Per cent.	Acid loaf. Per cent.
Water only	0.54	0.54
Pepsin digestion	6.34	7.45
Pancreatin digestion	4.00	3.71

BREAD DIGESTION EXPERIMENT NO. 2.

In further study of the effect of nitrite nitrogen on the digestive ferments, bread was baked from Pillsbury's Best flour (not bleached) according to our usual formula and also by substituting for a part of the water, water containing an amount of hydrochloric acid equivalent to ten cubic centimeters of decinormal acid together with an exactly equivalent quantity of sodium nitrite, and to a third loaf hydrochloric acid equivalent to 20 cc. of decinormal acid together with its equivalent of sodium nitrite.

The three loaves of bread were substantially the same in appearance, except that one containing the greater amount of nitrite was somewhat darker and both those containing acid were slightly larger than that containing no acid. The acidity of the bread as baked was determined and found to be 0.13 per cent. for the loaf containing no acid, 0.12 per cent. for each of the other two calculated as lactic acid; and the amount of nitrite nitrogen in the bread was found to be a trace for that to which no nitrite was added and 3.0 parts per million for each of the other two. The digestion was carried out as in bread experiment No. 1 except that 0.020 gram of pepsin was used to each 20 grams of bread. In the table given the loaves are designated by the actual amount of nitrite nitrogen added to the bread as calculated upon the flour used, which in the case of the 10 cc. acid loaf was 40 parts per million and for the 20 cc. loaf 80 parts per million.

The amount of protein extracted from the bread is calculated in per cent. of the moist bread taken for digestion.

	Plain loaf.	40 parts nitrite loaf.	80 parts nitrite loaf.
Water extract	0.52	0.44	0.49
Pepsin extract	6.0	5.40	6.06
Pancreatin extract	3.9	4.0	4.60

BREAD DIGESTION EXPERIMENT NO. 3.

This experiment was made exactly similar to experiment No. 2. Four loaves were made: one without acid and nitrite, the others with hydrochloric acid and nitrite equivalent to twenty, thirty and forty cubic centimeters of decinormal acid respectively, and containing nitrite nitrogen expressed in parts per million of the flour as follows: 80, 120, 160. The loaf containing the greater amount of nitrite was somewhat smaller than the other three, much darker in color when cut, and had a peculiar unpleasant odor. The other two loaves were also perceptibly darker than that without nitrite. The determined acidity of all loaves was the same, 0.12 per cent. expressed as lactic acid for the moist bread. The nitrite nitrogen present expressed as parts per million of the moist bread was as follows: trace, 2, 5 and 12 parts per million. All the breads contained substantially the same amount of moisture. The protein obtained from the bread by the water, pepsin and pancreatin liquids was as follows:

	Water.	Pepsin.	Pancreatin.
Loaf with no nitrites	0.72	4.50	3.64
Loaf with 80 parts per million	1.00	5.20	4.16
Loaf with 120 parts per million	1.20	4.80	4.16
Loaf with 160 parts per million	1.12	4.52	4.04

Each of these four breads after being grated were put in fruit jars and on the fifth day after baking all had many small colonies of mold started in various parts of the mass, the condition for each bread whether containing nitrites or none being substantially the same.

The solids in solution after the digestion in bread digestion experiments Nos. 2 and 3 were determined by evaporating 10 cc. of each solution to dryness in a weighed porcelain dish. The weights of the residue for the 10 cc. are given in table below:

Experiment No. 2. Added nitrites:	Water.	Pepsin.	Pancreatin.
No nitrites	0.066	0.136	0.460
40 parts nitrite nitrogen	0.073	0.133	0.471
80 parts nitrite nitrogen	0.075	0.142	0.495
Experiment No. 3. Added nitrites:			
No nitrites	0.062	0.100	0.297
80 parts nitrite nitrogen	0.067	0.131	0.142
120 parts nitrite nitrogen	0.072	0.110	0.137
160 parts nitrite nitrogen	0.085	0.120	0.230

The somewhat remarkable results with the pancreatin in experiment No. 3 were verified by a second trial with results almost identical with the first.

BREAD DIGESTION EXPERIMENT NO. 4.

Bread showing faint trace of nitrites was grated and divided into 20-gram lots for digestion as in other experiments. 200 cubic centimeters of 0.3 per cent. HCl and 20 milligrams pepsin were used with and without sodium nitrite. A test with plain water and pepsin, water only, and hydrochloric acid only was carried on at the same time. The amount of sodium nitrite used was 0.001, 0.010, 0.050 and 0.100 gram equivalent to 10, 100, 500 and 1000 parts per million nitrite nitrogen calculated on the bread. The protein in solution expressed in per cent. of bread and calculated from the nitrogen determined was as follows:

	Per cent.
Water and bread only	0.64
Hydrochloric acid and bread only	0.80
Bread, pepsin and water	0.8
Bread, pepsin, hydrochloric acid	5.66
Bread, pepsin, hydrochloric acid and 0.001 gram sodium nitrite.	5.38
Bread, pepsin, hydrochloric acid and 0.010 gram sodium nitrite.	5.79
Bread, pepsin, hydrochloric acid and 0.050 gram sodium nitrite.	5.18
Bread, pepsin, hydrochloric acid and 0.100 gram sodium nitrite.	4.51

BREAD DIGESTION EXPERIMENT NO. 5.

A sample of bread bought in the open market and which contained only a trace of nitrite nitrogen was grated as in other trials and weighed into lots of 20 grams each, and digestion experiments with pepsin were made in duplicate using 100 mg. pepsin and 200 cubic centimeters of liquid to each lot. One lot contained pepsin, water and bread only. Another contained hydrochloric acid equivalent to 0.15 per cent. of the liquid used; and in three others this equivalent of hydrochloric acid was replaced entirely, one-half replaced and one-fourth replaced by dissolving in water nitrogen peroxide produced by blowing air freely through the gases resulting from the action of nitrous acid on ferrous sulphate.

The total acidity of this liquid was equal to 42.5 cubic centimeters decinormal alkali for 100 cubic centimeters, and 100 cubic centimeters required 32.0 cubic centimeters decinormal potassium permanganate to oxidize it. This shows the presence of 16 cc. of decinormal nitrous acid in each 100 cc. and by difference we find 26.5 cc. of decinormal nitric acid present. 200 cc. of the acid solution contained an equivalent of 32 cc. decinormal nitrous acid containing 0.0448 gram nitrite nitrogen which, calculated to the twenty grams of bread used, was equivalent to 2240 parts nitrite nitrogen per million. In those tests in which the one-half and the one-fourth quantities nitrogen acids were used there were present 1120 and 560 parts per million nitrite nitrogen acid calculated on the bread.

The digestion of all the samples of bread was allowed to continue at 38° C. for one hour, at the end of which time all were allowed to filter for one hour, when 10 cubic centimeters of each solution were taken for determination of nitrogen. At the end of one-half hour's time it was evident from the appearance of the bread that all of those in which acid was present were digesting rapidly. No difference in appearance could be detected except that the contents of those flasks containing all nitrogen acids were of a pale lemon-yellow color. Those containing one-half nitrogen acids were distinctly less yellow, those containing one-fourth nitrogen acid were only slightly colored, and those containing only hydrochloric acid were uncolored. The filtered liquid from all these four lots gave well marked biuret reaction.

The average amounts of protein in solution as determined from the nitrogen and calculated as per cent. of bread were as follows:

	Digested protein. Per cent.
Water, pepsin and bread	1.36
Nitrogen acids, pepsin and bread	7.44
$^1/_2$ nitrogen acids, pepsin and bread	8.36
$^3/_4$ nitrogen acids, pepsin and bread	9.00
Hydrochloric acid, pepsin and bread	8.75

FLOUR DIGESTION EXPERIMENT NO. I.

This experiment is similar in all particulars to bread digestion experiment No. 4, except that 20 grams of flour, unbleached and containing no nitrite, were used in place of bread. The results obtained are calculated as protein (N × 5.7) in per cent. of the flour used.

	Per cent.
Flour and acid only	7.94
Flour, water and pepsin	2.69
Flour, acid and pepsin	11.13
Flour, acid, pepsin and 0.001 gram sodium nitrite	11.00
Flour, acid, pepsin and 0.010 gram sodium nitrite	10.72
Flour, acid, pepsin and 0.050 gram sodium nitrite	11.13
Flour, acid, pepsin and 0.100 gram sodium nitrite	10.94

FLOUR DIGESTION EXPERIMENT NO. 2.

In this experiment the same flour not bleached, bleached by Alsop process 3 times, 6 times and 18 times, and strongly bleached by nitrosyl chloride was treated by digestive fluids just as was the bread in bread digestion experiment No. 2. 20 grams of the flour were used, and the amounts of nitrite nitrogen present were 0, 2, 5, 15 and 0.3 parts per million. The results show digested gluten in per cent. of protein on the flour and also the total solids in solution as found by evaporation, and calculated as per cent. of flour.

PEPSIN DIGESTION.	Solids in solution.	Protein in solution.
Not bleached	15.26	9.66
3 times bleached	15.42	9.98
6 times bleached	15.96	9.75
18 times bleached	16.25	9.63
Nitrosyl chloride bleached	15.89	9.66
PANCREATIN DIGESTION.		
Not bleached	20.78	9.34
3 times bleached	19.96	8.70
6 times bleached	21.28	9.70
18 times bleached	20.06	9.47
Nitrosyl chlorid bleached	21.28	9.12

FIBRIN EXPERIMENTS.

Halliburton made use of Grutzner's method of comparing digestibility to show that nitrites inhibited the digestibility of fibrin by pepsin. This method depends upon the color imparted to the digestive fluid by digesting fibrin which has been stained with carmine. That this method does not furnish reliable data in the presence of nitrites is apparent from the following:

Fibrin was obtained from ox blood by heating the coagulated blood in salt water until the blood coloring matter had entirely disappeared. This finely divided fibrin was then stained with cochineal (carmine) dried between blotters and weighed.

A series of three experiments was run, each containing 0.6 gram fibrin and 10 cc. of digestive fluid (0.06 gram pepsin in 100 cc. 0.2 per cent. HCl). To one was added 2 cc. of water, to another 1 cc. $NaNO_2$ solution (0.125 gram in 100 cc.) and 1 cc. of water, containing therefore nitrite nitrogen equivalent to 20 parts per million. To the third was added 2 cc. of the sodium nitrite solution equivalent to 40 parts nitrite nitrogen per million. After $5^1/_2$ hours the same amount was found digested in each (a very small residue being left) but the color in those containing $NaNO_2$ had become orange or almost yellow, while the one without nitrite was a deep crimson. In water solution alone it was found that nitrites quickly destroyed the color of carmine. A small amount of nitrite added to a part of the digested solution in the blank soon changed the color from red to yellow. This error of Prof. Halliburton[5] was pointed out by us to the several experts in the Kansas City trial, including Prof. Rockwood,[8] at the time that we sent them our method of making these digestive tests early in 1910.

In these experiments the digestion was allowed to continue for 17 hours as in the experiments made by Halliburton. At the end of this time all solutions were filtered and equal portions of each filtrate taken for estimation of digested fibrin from nitrogen determined by the Kjeldahl method. The results were as follows, expressed in grams of fibrin in solution:

Amount of nitrite.	Fibrin digested. Gram.
None	0.184
20 parts nitrite nitrogen per million	0.189
40 parts nitrite nitrogen per million	0.189

While recognizing the fallacy of the above several experiments as to their bearing upon the bleached flour controversy because of the use of sodium nitrite, nitrous and nitric acids (which do not exist in commercially bleached flour) we have carried on these experiments to show the errors in the work and conclusions of Ladd,[2] Halliburton,[5] Mann[6] and Hale.[7] It naturally will be seen that the animal experiments conducted by Hale[7] wherein he used large quantities of sodium nitrite, nitrous and nitric acid, both internally and by subcutaneous injection, have no bearing upon the question as to what the deleterious effect might be of the so-called nitrite-reacting material in flour. The samples of flour which he treated in his laboratory did not represent the commercial operation of bleaching flour, and we know from experiments that we have conducted along this line that flour treated with oxides of nitrogen to the extent as given by this experimenter would be wholly unfit for commercial purposes and would not pass even the ordinary crude flour inspection. We have for a long time recognized that an entirely different substance is produced in bleached flour during the process of bleaching by nitrogen oxides and similar substances.

It is not our purpose at this time to go into the detailed experiments which we have made on this phase of the subject, but only to call attention to some of the more important facts bearing on the chemistry of decolorizing the natural color of flour.

In a previous article,[1] we called attention to the fact that the coloring matter of flour is of the same nature if not identical with carotin, and we have carried on a large number of experiments upon these coloring matters to determine their character. We have satisfied ourselves that they are practically identical in all particulars and are chemically associated with a large class of colors widely distributed in nature, among which may be mentioned the coloring matter of pumpkins, palm oil, June butter, and naturally the grasses from which June butter is produced. We have in various ways made compounds of this coloring matter with nitrogen oxides, nitrosyl chloride and similar agents, and have again recovered not only the mineral agents with which the coloring matter was treated, but in some cases the coloring matter itself.

This property of uniting directly with nitrogen oxide, nitrosyl chloride, etc., is a well-known characteristic of terpenes. We have found, too, that the compounds formed with oxides of nitrogen and certain terpenes respond to the Griess reagent, just as does the compound formed by the coloring matter of flour with oxides of nitrogen and nitrosyl chloride. In both cases the reaction in the development of the characteristic pink produced by the Griess reagent develops more slowly than when an equivalent amount of inorganic nitrite or nitrous acid is used. We might also mention in this connection that certain nitroso bodies, such as nitroso phenol, also respond to the Griess reagents for nitrites. These reactions indicate that the Griess reagent will take up the NO group from these compounds and react with it in the same manner as though it were a nitrite.

The coloring matters above mentioned, whether distributed as they are in food products, or in a suitable solvent such as chloroform, or in the pure crystalline condition, take up nitrogen oxides with great avidity, being in this nature akin to basic substances. We have found that the nitrogen oxides which are always present in the air combine with this coloring matter much as they do with the alkaline residue which remains in alkali starches, and that such starches when exposed to the air take up appreciable quantities of nitrite nitrogen and respond to the Griess reagent. When flour is exposed to ordinary air it takes up readily the nitrogen oxides and becomes bleached just as it does when exposed to the gases of the electric bleaching machine. Evidently the artificial aging of flour is identical with the natural aging which has been going on ever since white flour was produced. This explains why flour in well ventilated warehouses and bakers' storehouses age more rapidly than when stored under other conditions. Flour which we have exposed to the outside air and to the air of living rooms we have found aged very rapidly. When exposed in the kitchen the yellow color will disappear within 24 to 48 hours, and the extent of nitrite nitrogen taken up may be in excess of the average one part per million which is found in flours which have been bleached by the electrical process.

In one experiment which was conducted, we have found as high as four parts per million nitrite nitrogen in flour thus bleached. A sample of alkali cornstarch, which was packed in a carton and sealed with a paper wrapper, took up nitrite-reacting nitrogen to the extent of 3.85 parts per million after standing for about five weeks in a well ventilated living room. We have even found that bread from unbleached flour exposed to the air of a kitchen over night contained more nitrite nitrogen in the morning than did fresh bread baked in the same manner from a flour which had been artificially bleached with nitrogen oxides.

It is our purpose in a future article to give the results of these experiments in detail, and to show the actual composition of the coloring matter itself. This much is given as being essential to the line of thought which we wish to bring out in our present article.

Having shown the nature of the compound in bleached flour, and that it responds to the nitrite reaction with the Griess reagent, and as no experimenter up to this time has proved the presence in commercially bleached flour either of sodium nitrite, nitrous or nitric acids, we feel justified in believing that the so-called nitrite reaction in bleached flour is due to this compound. The purified coloring matter of flour combines with comparatively large amounts of oxides of nitrogen and nitrosyl chloride, as we have repeatedly demonstrated in our experiments on weighed quantities of the coloring matter. We have further proved in trials where bleaching was being practiced on a commercial scale that in nearly all instances one pound of liquefied nitrosyl chloride gas will bleach 1000 barrels of flour, and often as high as 2000 barrels. Knowing then the chemistry of bleaching flour, it will be recognized at once that if there is any toxic substance in the flour it must be due to this substance, and any and all animal experiments which have been conducted by the several experimenters using sodium nitrite, nitrous or nitric acids from whatever source obtained, have no bearing whatever on the true chemistry of bleaching nor upon the toxic effect which the substance developed may have upon animals. Extensive experiments which we, Haines,[9] Wilcox and Luff,[10] Hale,[11] and others have conducted in feeding bread and extracts from commercially bleached flour have failed to show any indication of a toxic or pathologic effect upon animals consuming the same. Further than this Vaughan[12] has experimented with the coloring matter containing the NO group which is produced in the bleaching of flour. He took 2 pounds of unbleached flour and extracted this with 2 liters of petroleum ether. The ether was separated by filtering and then through this was passed a current of oxides of nitrogen prepared by the action of nitric acid on copper. The coloring matter held in solution was bleached and precipitated. The precipitate was collected and washed with petroleum ether. Practically the whole of this precipitate was introduced into the stomach of a rabbit which had been kept fasting for two days. This had no recognizable effect on the rabbit, nor did it alter the spectroscopic appearance of its blood. The substance gave Liebermann's nitroso test.

CONCLUSIONS.

Nitrites do not interfere with diastase in its action on starch, even when present as sodium nitrite to the extent of one part in 1000.

Nitrous and nitric acid do not inhibit the action of peptic digestion, and may wholly replace hydrochloric acid in this essential first stage of digestion, while digestion by pepsin without acids will not take place.

While pancreatic digestion will not take place in the presence of free acids, it is not inhibited by the presence of relatively large quantities of nitrites, nor is its action restrained on the proteid which has been previously subjected to appreciable quantities of nitrous and nitric acids.

No experiments by the several writers on this subject have demonstrated the presence in commercially bleached flour of either mineral nitrite, nitrous or nitric acids.

The nitrite-reacting material of flour, as far as we have been able to determine, is entirely due to the direct union of the coloring matter and the nitrogen oxide.

Vaughan has shown that the substance which gives the nitrite-reacting material and which responds to Liebermann's nitroso reaction is not poisonous nor does it have any action on the blood.

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2. Ladd and Bassett, *Journal of Biological Chemistry*, **6**, 75 (1909).
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4. Wesener and Teller, *American Food Journal*, Sept. 15, 1907. Testimony given before Judge Pollock, State Court, North Dakota, October, 1908.
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RESEARCH DEPARTMENT,
THE COLUMBUS LABORATORIES,
CHICAGO.

SOME OBSERVATIONS UPON THE ASSAY OF DIGESTIVE FERMENTS.

By HOWARD T. GRABER.

Received October 3, 1911.

The digestive ferments have many characteristics peculiar, for the most part, solely to themselves.

PEPSIN.

These various characteristics are well illustrated by the enzyme pepsin, and to explain I wish to present the following experiment. As is well known the U. S. P. test for pepsin reads as follows: "Immerse a hen's egg, which should be *fresh*, etc." Certainly this wording seems sufficiently simple, plain and explicit, but in reality it becomes evident to any one conducting a long series of tests, that the words "fresh eggs" are decidedly loose and inaccurate.

The "fresh egg" of the housekeeper and epicure may successfully pass the test of a sensitive palate and yet prove unsuited for the purpose here.

This then halts us at the beginning of our experiment to ask "what constitutes a fresh egg, and do all fresh eggs give concordant results?"

To answer this question I collected 21 eggs from a number of chickens. The eggs had all been laid on the same day and the chickens all belonged to one man and had been kept under the same conditions for months. With these eggs, I tested two samples of pepsin, one marked 1 : 3000 and the other 1 : 10,000, starting the test on the second day after the eggs had been laid and continuing every following day up to and including the 10th, with the following results.

The tests clearly demonstrate the fact that an egg may be fresh and give an assay which varies from one to two thousand units. One chemist working with eggs two days old would assign a digestive activity to a sample of pepsin from one to two thousand units lower than another chemist working under exactly similar conditions, but using eggs which were five to six days old. I should, therefore, like to suggest that when chemists are assaying pepsin that they satisfy themselves as to the age of the eggs which they are using before proceeding with the test. Eggs, however, do not always give the highest result between the 5th and 7th day, but it is safe to say that on an average, eggs which are between 5 to 7 days old give the maximum activity to a sample of pepsin.

The effect of the age of the egg is particularly noticeable in the case of the 1 : 10,000 pepsin where the residue on the 2nd day eggs was 3 cc. and on the 5th day had decreased to $^6/_{10}$ of one cc.; and after the 5th day the residue started to increase until on the 10th day it was the same as on the 2nd day.

The above experiment illustrates how sensitive the pepsin is to the nature of the albuminoid upon which it is acting.

To show how reactive it is to environment it is interesting to note that the activity of pepsin is not only inhibited in neutral solution, but in proceeding to the alkaline reaction the pepsin is soon destroyed, and even in an acid menstruum in which the pepsin normally is most active, a difference of 0.025 per cent.

Laid on 31st. Sample No.	Strength tested for.	April 3rd. 2 days.		April 4th. 3 days.		April 5th. 4 days.		April 6th. 5 days.		April 7th. 6 days.		April 8th. 7 days.	
		Residue.	Strength.	Residue.	Strength.	Residue.	Strength.	Residue.	Strength.	Residue.	Strength.	Residue.	Strength.
Number 1	1 : 3,000	0.8 cc.	—	0.5 cc.	—	0.3 cc.	—	0.3 cc.	—	0.4 cc.	—	0.6 cc.	—
Number 1	1 : 3,250	1.0 cc.	1 : 3,250	0.6 cc.	—	0.4 cc.	—	0.4 cc.	—				
Number 1	1 : 3,500	$1\frac{1}{4}$ cc.	—	0.9 cc.	1 : 3,500	0.7 cc.	1 : 3,500+	0.6 cc.	1 : 4,000	0.6 cc.		1.0 cc.	1 : 3,500
Number 1	1 : 4,000									1.0 cc.	1 : 4,000	$1\frac{1}{2}$ cc.	—
Number 2	1 : 10,000	3.0 cc.	—	$2\frac{1}{2}$ cc.	—	$1\frac{1}{2}$ cc.	9,000	$^6/_{10}$ cc.	1 : 10,000	$^8/_{10}$ cc.	1 : 10,000	2 cc.+	—
Number 2	1 : 8,000	$2\frac{1}{2}$ cc.	7000	$1\frac{1}{2}$ cc.	7000+	$^7/_{10}$ cc.	—	$^4/_{10}$ cc.	—	$^6/_{10}$ cc.	—	1 cc.	8,000
Number 2	1 : 6,000	$^9/_{10}$ cc.		$^6/_{10}$ cc.		$^5/_{10}$ cc.	—	$^3/_{10}$ cc.	—	$^3/_{10}$ cc.	—	$^4/_{10}$ cc.	—

acid more or less than 0.309 per cent. shows a variation in the amount of albumen digested, and 0.05 per cent. more or less acid will show a difference of 3 cc. in the residue.

Some chemists who have observed the variations in the assay of this enzyme have sought a remedy in the use of dried egg albumen, but if the albumen in the moist stage gives such wide variations when used for assay, the dried albumen must of necessity do the same. I should, therefore, recommend that each individual adopt a standard pepsin which has been assayed by eggs of different age, and then check all future samples against said standard.

PANCREATIN.

Another enzyme showing the same peculiar characteristics as pepsin is pancreatin.

Pancreatin is a combination of trypsin, amylopsin and steapsin, together with myopsin and more or less extraneous matter.

The Pharmacopoeia gives two assays for this preparation, one of which measures its proteolytic or tryptic strength and the other its amylolytic or starch hydrolyzing power. The milk or trypsin test has not proven satisfactory in my hands and I consider the test too rigid. The difficulty seems to be in what is meant by the wording "*some* nitric acid," also as of what a "coagulation" consists, and where coagulation ceases and separation and precipitation commence. Inasmuch as pancreatin, if taken internally, is used for its starch hydrolyzing power, and its tryptic enzyme would be killed in passing through the stomach, most manufacturers to-day do not apply the milk test at all. The tryptic strength can be of value only in the preparation of pre-digested foods.

The other assay which measures the amylolytic strength gives very satisfactory and concordant results, but amylopsin, and in fact, all diastatic enzymes do not react the same upon all kinds of starch. Although cornstarch is official, it is interesting to note that many manufacturers use potato starch in assaying diastasic ferments, and a great variation exists in the strength of a diastase when stated in terms of potato starch or cornstarch. To be brief, I should say that pancreatic diastase shows $^1/_3$ more activity when tested upon potato starch than when tested upon cornstarch, or to state it in another way—a pancreatin which tests 1 : 50 in 10 minutes on potato starch would require 15 minutes when tested upon cornstarch under identical conditions. The great variation in gauging the color of the digested starch solution when added to the iodine can be prevented by all chemists checking the digestion until 4 drops of the digested starch solution cease to give any color whatever when added to the iodine solution.

A third test for pancreatin which is not official, but which I have used with good success, measures the strength of the steapsin or the fat-splitting enzyme present. The test is as follows:

Weigh out 5 grams of a 50 per cent. emulsion of almond oil into a small Erlenmeyer flask, add 25 cc. of a solution of sodium bicarbonate (20 grams to 8 ounces) (1 gram to 182 cc.). Mix thoroughly, place the flask in a water bath at 40° C. and let stand until the mixture is exactly 40° C., then add 0.1 gram ferment. Mix a second time, replace in the water bath and maintain at 40° C. for $^1/_2$ hour, gently inverting the flask every 5 minutes. At the end of 30 minutes' digestion, remove the flask from the water bath, transfer the contents to a beaker, heat to boiling and titrate the alkalinity with $N/10$ H_2SO_4 using phenolphthalein as an indicator. Run a blank at the same time. The difference between the alkalinity of the blank and the alkalinity of the sample to which the ferment was added represents the sodium bicarbonate neutralized by the free fatty acid liberated by the action of the steapsin.

RENNET.

The third important animal enzyme showing the peculiarities of these digestive ferments is rennet and the standard rennet on the market to-day is what is labeled as 1 : 30,000, which means that, assuming a standard milk gallon as weighing 60,000 grains, one grain of rennin will curdle $^1/_2$ gallon of milk (or 30,000 grains) in 10 to 12 minutes. This enzyme shows its selective characteristics as to the nature of proteid, temperature and reaction of media, and results sometimes vary when different samples of milk are used from different cows, but I have found that with the following method of procedure very concordant results are obtained.

In selecting the milk to be used I stipulate fresh milk and request that it has not been pasteurized or heated in any way. Two quarts of this milk are heated to 40° C. and to this is added 10 cc. of a solution of rennin containing 0.4843 gram in 150 cc. water. I never stir the milk, but mix the rennin by pouring from one receptacle to another. The time of mixing is noted and at $^1/_2$-minute intervals thereafter the milk is gently tipped to one side. By this means coagulation can be detected the moment it commences, and at the congealing point the milk should separate into a solid casein mass and liquid whey. I find that the best commercial samples congeal in 10 to 12 minutes.

PAPAIN AND BROMELIN.

As in the animal kingdom we have juices whose specific function is to tear asunder the food material to make it available for the needs of the body, so in the plant kingdom we find analogous enzymes whose function is exactly the same, that is, to render the plant's food assimilable.

Most important among these enzymes which man has appropriated to his use are bromelin and papain. Bromelin occurs in the juice of the pineapple, and papain the fruit of the paw-paw, a tree growing in the tropical countries of the Bahamas and the West Indies.

The paw-paw tree attains its full bearing capacity in a year. It produces from 40 to 50 paw-paws of a dark green color, ripening to a deep yellow. The shape and general appearance of the paw-paw fruit is very similar to a squash. In collecting the papain a very light superficial incision, not over $^{1}/_{8}$ of an inch in depth, is made in the fruit from which exudes a clear water-like juice, which on exposure to air becomes opaque. The milky fluid will run for a short time, but soon coagulates; when this takes place the coagulated juice is brushed off and a fresh incision made, thus producing another but smaller yield of juice. The scorings are thus made about $^{1}/_{2}$ inch apart all around the fruit and the tappings are usually made just previous to ripening.

The juice must be collected in porcelain-lined receptacles as it is very corrosive and would not only injure metal containers, but the use of such would injure the appearance and qualities of the papain. The peculiar property of this enzyme is its solvent action for raw beef and the natives knowing this property have utilized it to their advantage. Even the leaves of the tree contain the enzyme and these foreigners have long been known to wrap a tough piece of meat in the leaves when, after a number of hours' contact, the meat becomes quite tender.

Knowing its solvent action upon raw proteid led me to consider meat as a means of standardization of the enzyme, and to be assured that I was working with the pure product I experimented with the fruit itself.

Several large paw-paws were prepared as follows: The green rind was first pared off, then the pulp was sliced into halves representing the inner and outer pulp respectively, and the seeds were collected. The juice was then expressed from these three different parts of the fruit, and the following test was then made upon these different juices.

Amount juice. Cc.	Amt. acid 0.3 per cent. HCl Cc.	Amt. water.	Amount 0.1 per cent. $NaHCO_3$.	Part plant employed.	Amt. of beef. Gms.	Time of digestion. Hrs.	Residue. Cc.
10	75 cc,	none	none	juice	10	6	12
10	none	75 cc.	none	outer pulp	10	6	27
10	none	none	75 cc.	outer pulp	10	6	35
10	75 cc.	none	none	inner pulp	10	6	16
10	none	75 cc.	none	inner pulp	10	6	30
10	none	none	75 cc.	inner pulp	10	6	40
10	75 cc.	none	none	seeds	10	6	19
10	none	75 cc.	none	seeds	10	6	29
10	none	none	75 cc.	seeds	10	6	40

The test clearly illustrates two facts:

First: That in an acid solution the papain is the most active, the neutral media ranking second, and the alkaline third.

Second: That the enzyme of the juice of the outer pulp was much more active than that of the inner pulp or the seeds.

Upon the strength of the above test I herewith submit the test in full as applied upon papain.

Pass a quantity of round steak, which has been freed from all fat and gristle, through a meat chopper using the finest knife. Of this ground proteid carefully weigh 10 grams into a six-ounce bottle, weigh carefully 0.325 gram papain and brush into the bottle. Then add 85 cc. of 0.3 per cent. HCl, stopper the bottle, mix well so as to break up the chopped meat, place the bottle in a water bath at 52° C. and maintain at this temperature for 6 hours, gently inverting the bottle every 10 minutes. At the end of six hours' digestion remove the bottle from the bath and pour the contents into a graduated settling tube. Let stand $^{3}/_{4}$ of an hour and then read the amount of undigested proteid left which should not measure over 2 cc. A papain which meets this test is reported as possessing an activity of 1 : 30 in 6 hours.

Some manufacturers claim that the test should be conducted in an alkaline media and that egg albumen should be used instead of raw beef; but to me this seems as absurd as to claim that pepsin should te tested upon starch in an alkallne media. The vegetable enzymes show the same selective peculiarities as do the animal enzymes, and the fact that the juice from the fruit shows its maximum activity in a 0 3 per cent. hydrochloric acid solution acting upon raw beef leads me to recommend this test as best suited for the assay of either bromelin or papain.

CONCLUSIONS.

To summarize, then, these digestive enzymes require more than that ordinary skill and experience in their assay.

We have seen by the foregoing:

First: That the composition of the white of the egg, chemically and probably even physically, when used for the assay of pepsin, has a great bearing upon the apparent strength of this ferment. The albumen seems to be more difficult to digest the first twenty-four hours after the egg is laid and a change gradually takes place until after about five to seven days it has reached its maximum solvent condition. After this period its digestibility gradually diminishes.

Second: In the assay of pancreatin for starch hydrolysis, as well as all the diastasic ferments, the kind of starch used is of prime importance and in stating the strength of each it should be in terms of the particular starch employed.

Third: The papain seems to be equally active on any kind of raw beef when acting in an acid media, but if the character of the beef is changed as, for instance, by cooking, papain loses its solvent action upon the proteid; and

Fourth: Rennet is influenced, in testing its coagulating power, by

The condition of the milk, its chemical composition such as the presence and quantities of inorganic salts, particularly those of calcium,

The manner of mixing the rennet with the milk;

The brand of cows from which the milk is taken; and lastly

The temperature at which the milk was kept before using and during the test.

LABORATORY OF THE RAY CHEMICAL COMPANY,
DETROIT.

PLANTS AND MACHINERY

THE MANUFACTURE AND PERFORMANCE OF THE EDISON STORAGE BATTERY.

By Howard Lyon.

Received August 5, 1911.

Fifty years ago Planté demonstrated the possibility of using an electric current to do chemical work on plates immersed in an electrolyte and of obtaining a current again through reversal of the chemical process by connecting the plates by a conductor outside of the container. Such a cell behaves exactly as though it were some sort of a structure in which electricity could be stored as a reagent in a bottle, and thus it has become generally known as a storage battery. Until a very few years ago there had been no radical departure as to the nature of the plates and the electrolyte from the fundamental form assembled by Planté. The modern practical battery has continued to make use of lead plates and a sulfuric acid electrolyte.

The lead battery as developed since the time of Planté is open to serious objections, chief of which are the following: *First.*—Lead structures, by reason of bulk necessary for strength and a heavy electrolyte, make the weight of the battery excessive. *Second.*—The electrolyte (sulfuric acid) is intensely corrosive, and the nature of the liquid compels confinement in a fragile container. *Third.*—Physically the lead structures are weak and the pockets of lead oxide are weaker still. *Fourth.*—Secondary chemical activity is set up in a lead cell while standing partly discharged producing sulfate of lead instead of the useful oxides, so that in idleness there is a marked loss of electrical energy. *Fifth.*—The specific gravity of a troublesome electrolyte should be definitely maintained and the electrolyte should be rather frequently renewed. As a matter of fact the specific gravity of the electrolyte is constantly changing in the cycle of charge and discharge. *Sixth.*—Charging current exceeding a certain rather low amperage causes "buckling" of the plates. This loosens the oxide from the pockets and thus lessens the ampere capacity of the cell besides tending to produce short circuits. *Seventh.*—Such cells even in idleness must be charged at frequent intervals, for a discharged or partly discharged cell disintegrates rapidly.

Realizing the very great importance of the storage cell in modern electrical development and also the imperfections of existing types of batteries, Mr. Edison, about ten years ago, set himself to the task of producing a storage cell in which if possible the defects noted above might be eliminated.

Stated briefly the Edison Storage Cell makes use of steel grids holding perforated tubes containing nickel oxide and nickel flake for the positive plates and perforated box-like cases containing iron oxide for the negative plates, the plates being immersed in a solution of caustic potash containing a small per cent. of lithium hydrate enclosed in a steel can. All the steel parts are protected by a specially durable nickel plate.

Commercial use of the later forms of the alkaline battery has abundantly demonstrated its practical efficiency for pleasure vehicles, trucks, and even omnibuses and cars. Chemical and structural durability is a phase of large significance as applied to this new energy-storing device. Durability and dependability are far more important qualities from the standpoint of the users of a storage battery than weight, cost, or efficiency, however desirable these latter qualities may be. *The truckman needs power not efficiency curves.* Durability is ensured by the mechanical construction of the Edison battery and by an electrolyte and active materials which remain unchanged with very moderate care. Dependability follows from the fact that in commercial service such treatment as a battery ordinarily receives will not change the nature or behavior of plates or electrolyte. The confidence of the manufacturers of the Edison battery is expressed by their guarantee that the capacity of the battery will be not less than 90 per cent. of the original capacity after three years of service when applied to commercial vehicles.

Commercial service inevitably means a likelihood of overcharge and discharge, and lack of attention to the electrolyte. This neglect in the Edison battery results merely in less immediate capacity, not in ruination of the cells.

Mechanically the cells are as stable as a well-made gas-cock. In fact they are so well made that the plates are confined in a container whose cover is welded in and all but hermetically sealed.

With renewal of electrolyte after each 250 complete charges and discharges, and addition of pure water from time to time to the electrolyte to make up for loss principally at the time of charging, and regulation of charging current according to experience based on careful recorded observation, there is no reason why the cells should not remain practically unchanged through a series of years. Combined with these qualities its weight, which is about half that of existing lead batteries of the same capacity, is such that a battery of sufficient capacity to propel a pleasure vehicle one hundred and fifty miles may be incorporated in what appears to be the natural and artistic body of the vehicle. In fact the electric pleasure vehicle has distinctly the appearance of a horseless carriage.

The Edison storage cell is at present being made in five sizes known as A-4, A-6 and A-8 together with two sizes for light work known as B-2 and B-4. These sizes differ only in the provision for active material and plate surface. The increase of weight for larger sizes is somewhat less than the increase of energy output. The following table gives the dimensions, weights, discharge rate and ampere-hour output for the three larger sizes:

	A-4.	A-6.	A-8.
Outside measurement of can in inches........	$2^9/_{16} \times 5^1/_8 \times 12^3/_8$	$3^3/_4 \times 5^1/_8 \times 12^3/_8$	$4^7/_8 \times 5^1/_8 \times 12^3/_8$
Weight of complete cell in pounds.......	13.3	19.0	25.0
Normal discharge rate in amperes.........	30	45	60
Rated ampere hour output...	150	225	300

These three types of cells have each the same height and require for clearance of pole pieces and connectors a compartment whose height is fifteen inches.

The following description which is distinctive for plate surface only, relates to a cell of type A-4.

All of the steel parts used for assembling the active elements as well as the can itself and the connecting bolts, nuts and washers are nickel-plated. After the plating process the parts are placed in sealed carbon-lined retorts arranged for the passage through of hydrogen gas during the process of annealing, which is accomplished with intense heat. By this process the nickel-plating is incorporated as a firm part of the steel surface itself. No amount of bending will cause it to peel. For both positive and negative plates the frames or grids for holding the cases containing the active materials are blanked out of sheet steel, leaving openings of such size as to accommodate the required number of cases. The positive plate consists of thirty tubes in two rows These tubes are about four inches long and one-fourth of an inch in diameter and are made of spirally rolled perforated steel ribbons, lapped and locked at the edges and reinforced by steel bands. The perforations in the walls of the tubes permit the moistening of the nickel hydrate with the electrolyte. The ends of the tubes are flattened so that they may be assembled and clamped down by tongues on the steel grid.

The filling of the tubes for the positive plate is a most interesting one and is a triumph of inventive ingenuity. Machines have been designed to automatically fill rows of tubes and tamp the nickel hydrate and flake nickel which are fed in alternately in such quantities as to make layers approximately $^1/_{100}$ of an inch in thickness for the nickel hydrate and a less thickness for the nickel flake. The nickel hydrate which is in no large measure conductive is thus brought into intimate reach of current action by thin layers or disks of nickel. In testing the distribution of active and conducting material a number of tubes are selected at random from a certain output. Cross-sections are made and the conductivity or contact of nickel flake with the walls of the tube is determined by use of a microscope and a metal stylus which is touched to successive layers with the result that an indicator gives proof of connection. Thus the number of poor connections is determined and counted. The filling is so carefully done that contact is ensured in 97 per cent. of the layers. The flake-nickel is prepared as follows: With a total thickness of a sheet of paper two hundred and fifty alternate layers of copper and nickel are deposited electrolytically on rotating drums shifted by traveling cranes. These cylindrical sheets are stripped off and cut up into squares about one-sixteenth of an inch in diameter. The squares are treated with ammonia in a retort and the copper dissolved and leaving only the very thin nickel flakes. The nickel flakes when washed and dried is so light that it floats in the air. There are 300 nickel hydrate units in each tube, 9000 in each plate and 36000 in an A-4 cell.

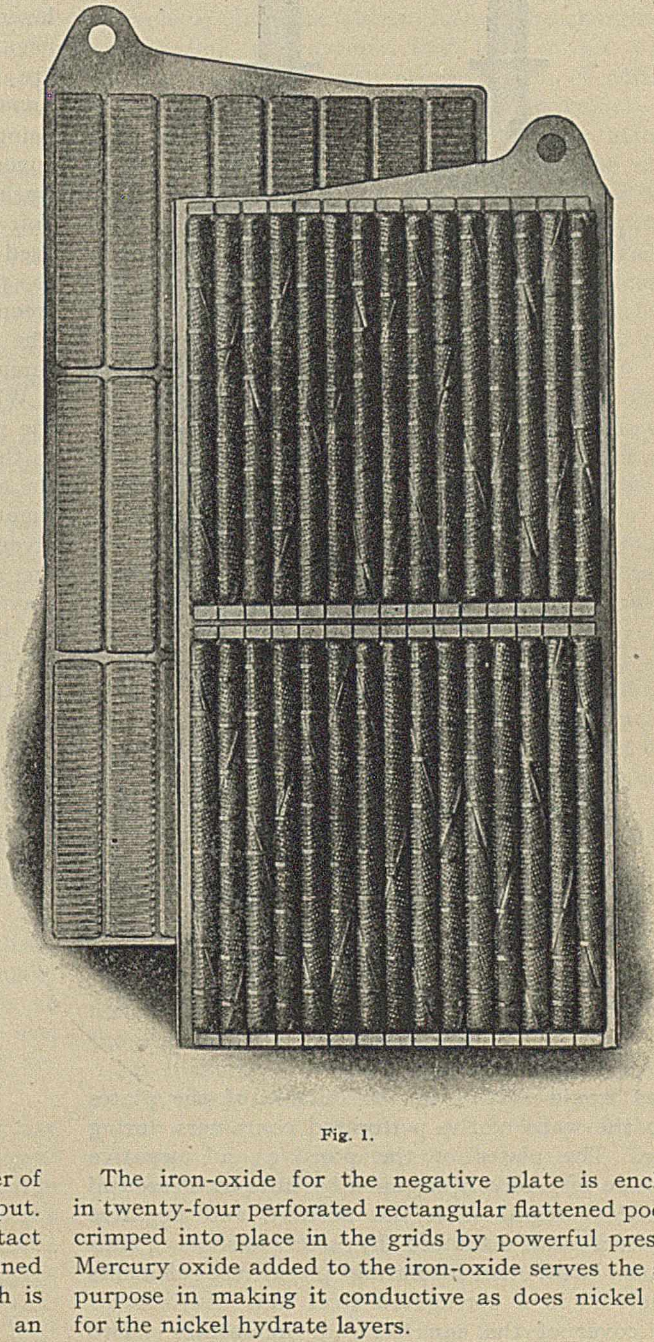

Fig. 1.

The iron-oxide for the negative plate is enclosed in twenty-four perforated rectangular flattened pockets crimped into place in the grids by powerful pressure. Mercury oxide added to the iron-oxide serves the same purpose in making it conductive as does nickel flake for the nickel hydrate layers.

The grids as assembled above are very light and strong, suited to withstand all shocks to which such a structure would be subjected in commercial use. Each cell of the A-4 type contains four positive and five negative plates assembled alternately with the negative plates outside. Hard rubber rods are used to space the plates. Rubber pieces also insulate the plates at the sides, edges and bottom from the steel can. The pieces of broad hard rubber at the bottom lift the plates enough above the steel surface to make a space for sediment, although in the Edison cell any deposit at the bottom of the cell will be almost wholly such as would adhere to the outside of the plates and to the walls of the perforated containers during loading. The plates of the positive and negative groups are respectively fastened by nuts to horizontal steel rods integral with the positive and negative pole pieces and distanced by steel washers. Thus assembled with the insulating pieces the elements are enclosed in a corrugated steel can.

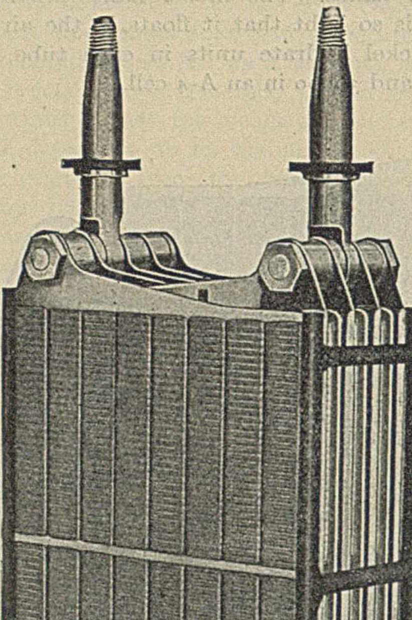

Fig. 2.

The cover of the can has four mountings. Two of the openings are of the pole pieces, a third for the separator valve which permits the escape of gas when charging but prevents spraying, evaporation, and the spilling of the electrolyte. The fourth opening is for the purpose of adding water to replace that carried off in charging and is fitted with a cover that may be clamped down and made water-tight by a locking lever. The positive and negative terminal posts are tapered to fit terminal lugs, the posts being insulated from the cover by hard rubber washers and bushings. Soft rubber packing is used about the terminals to prevent leakage or creeping of the salts. The packing ring is held down by a hard rubber nut threaded into a pocket of the cell cover.

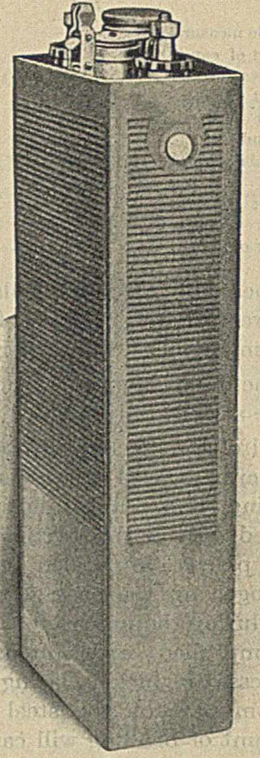

Fig. 3.

When the cover has been properly assembled with the plates in the steel can, it is welded at the edge to the can itself by the oxyacetylene flame, and thus the can is in effect, a box of seamless steel. The corrugations of the can give maximum rigidity for a given weight or thickness of material. The cells are assembled into a battery in strong bent-wood trays and insulated and spaced from one another by hard rubber buttons which extend through the sides of the trays and fit over embosses pressed out on the sides of the steel containers. Blocks in the bottom of the tray fit into the flanged bottoms of the cells from which they are insulated by soft rubber pads. Steel terminal lugs fit the tapered pole pieces and cells are electrically connected by nickel-plated copper links swedged into the lugs.

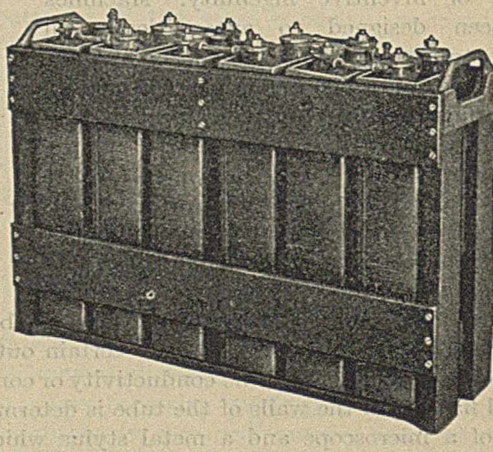

Fig. 4.

The A and B type of cells were evolved from the earlier type E in which flake graphite was used in the positive plate to make the active material conductive. The graphite slowly oxidized and swelled and the change resulted in a diminished capacity for the cell. In the later evolved battery conduction (in the positive plate) is secured as already stated by nickel flake. Although thousands of the type E cells had been put upon the market, the manufacture of these cells was discontinued for four or five years, during which time at an expense of over two million dollars many thousand experiments were made to improve the positive element. These experiments resulted in the nickel flake and hydrate unit previously described. Rarely indeed has inventive activity been applied more vigorously or persistently to overcome difficulties than in the case of this later development of a practical storage battery. Indeed this accomplishment, measured by the skill applied and the far-reaching value of the product, may well be rated as the crowning achievement of a great inventor.

A comparison of weights of lead cells and Edison cells of the same capacity without trays shows about one-half the weight for the latter type. The space occupied by an A-4 battery with its holder is somewhat less than that of a lead battery of equal energy capacity.

Less dead weight to be carried and less space requirement for battery means a vehicle of lighter construction and consequently greater mileage capacity for the lighter and less bulky type. The normal working voltage of the Edison battery is 1.2 as compared with 1.96 volts for the lead cell. Hence for a given voltage the number of cells of the Edison and lead type required would be as 13 to 8. In the comparisons of weight and bulk this fact has of course been taken into consideration.

The first cost of a lead battery is less than that of the Edison type, but when durability is taken into consideration the added cost of renewals and maintenance for the lead battery would make a total much exceeding the initial cost of an Edison battery. Users of lead batteries have been troubled by the fact of a steadily lessening capacity with even one year's use. The Edison battery is guaranteed to retain practically its initial capacity after three years of service, such as is required in trucking.

The nature of the care required for the Edison battery is simply addition of distilled water to make up for charging loss, the renewal of the solution at infrequent intervals and charging according to use. No attention *can* be given to the plates for they are entirely inaccessible.

The lead battery must be charged whether in use or idleness. Charging a lead cell beyond its normal rate causes rapid deterioration. The rate of charge for an Edison cell is practically limited only by the temperature developed which should not exceed 105° F. The limited mass in plates and electrolytes of course makes the regulation of the charging rate necessary. However, the steel cans transfer heat to surrounding air while the containers for the lead type are heat insulators.

The Edison cell has a somewhat higher resistance than the lead cell, and for this reason in hill-climbing the lead cell would have a seeming advantage in the fact that it would be possible to call upon the battery for greater current to carry the vehicle over the hill. This is only a seeming advantage, for the Edison cells and vehicle may be lighter, so that there will be less work to do and further the lead battery is structurally limited in its current output. An overcharge is distinctly destructive to its elements.

It means little to say that the lead cell is more efficient pound for pound when *new*, for the cell does not retain the initial advantage long after it is put in service. It is harassing to a user of an electric vehicle not to be able to hasten the charging rate to complete a journey. The Edison cell permits this treatment and even shows a gain of efficiency. Futhermore, the driver of an electric vehicle using the Edison battery may definitely know before he starts on his journey whether or not the current will hold out. With a given charge he is able to depend upon a given capacity by reason of the dependable character of the battery. A feature of value in relation to the Edison battery is that the capacity of the cells becomes greater with use. Overcharging expedites this betterment of the battery and is recommended by the manufacturers.

It would be manifestly out of place to attempt to discuss, within the limits of this article, the curves that have been plotted to show the behavior of the battery under various conditions favorable and unfavorable.

A full discussion of this subject may be found in the paper of Mr. Walter E. Holland read at the 26th annual meeting of Edison Illuminating Companies September 6–8, 1910.

An idea of the nature of laboratory tests as applied to the Edison battery may be obtained from the following description of typical curves and from conclusions based on the inspection of the curves. Effect of normal and overcharges for a battery after having covered 17,000 miles in a one-ton delivery wagon.

Plates Nos. 5, 6, and 7 show in a graphical way what happens to cells which have been subjected to various sorts of treatment, and especially to the treatment which has been known to be destructive to other types of storage cells. The legends accompanying the plates referred to show the nature of the laboratory test, and an inspection of the curves tells at a glance the result of various treatments.

An inspection of the curves of charge and discharge (Fig. 8) for an Edison cell shows an efficiency of 60 per cent. to 65 per cent. A new lead cell shows an efficiency of 75 per cent. to 80 per cent. but this efficiency falls off very rapidly when the cell is put into use, while the Edison cell shows a gain in efficiency. One particular Edison battery that had given a total of 20,000 miles in delivery service showed a gain in efficiency.

The statements of the writer as related to the lead

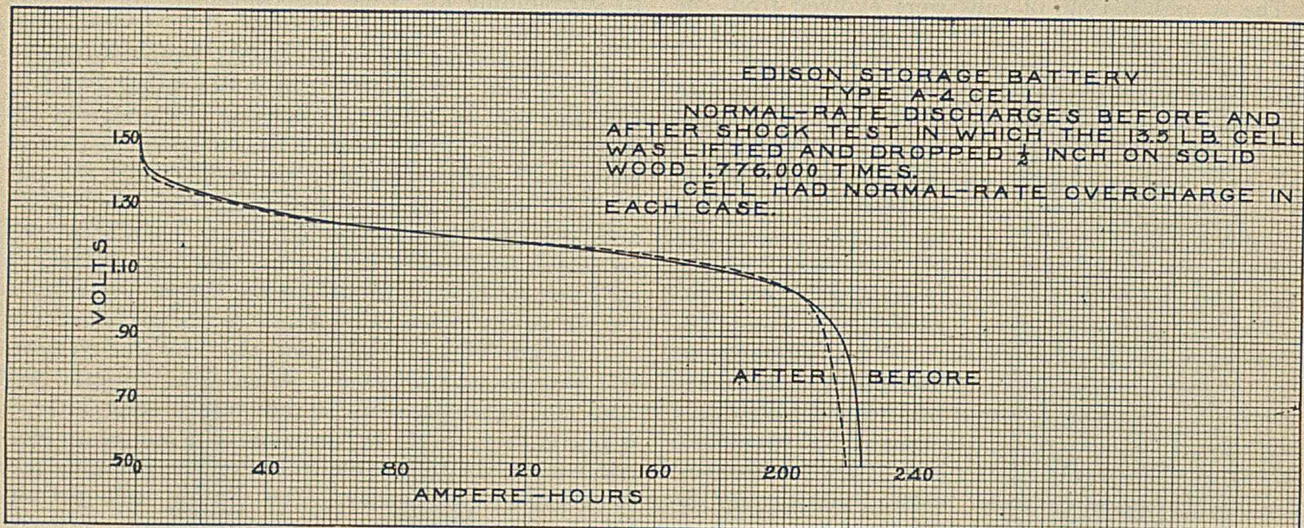

Fig. 5.

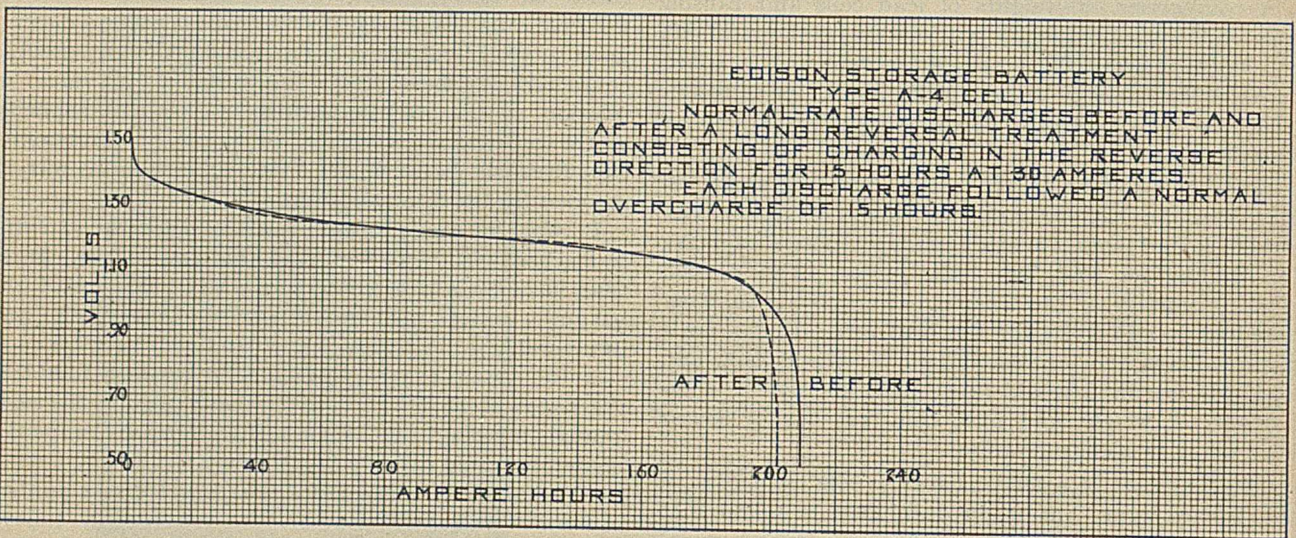

Fig. 6.

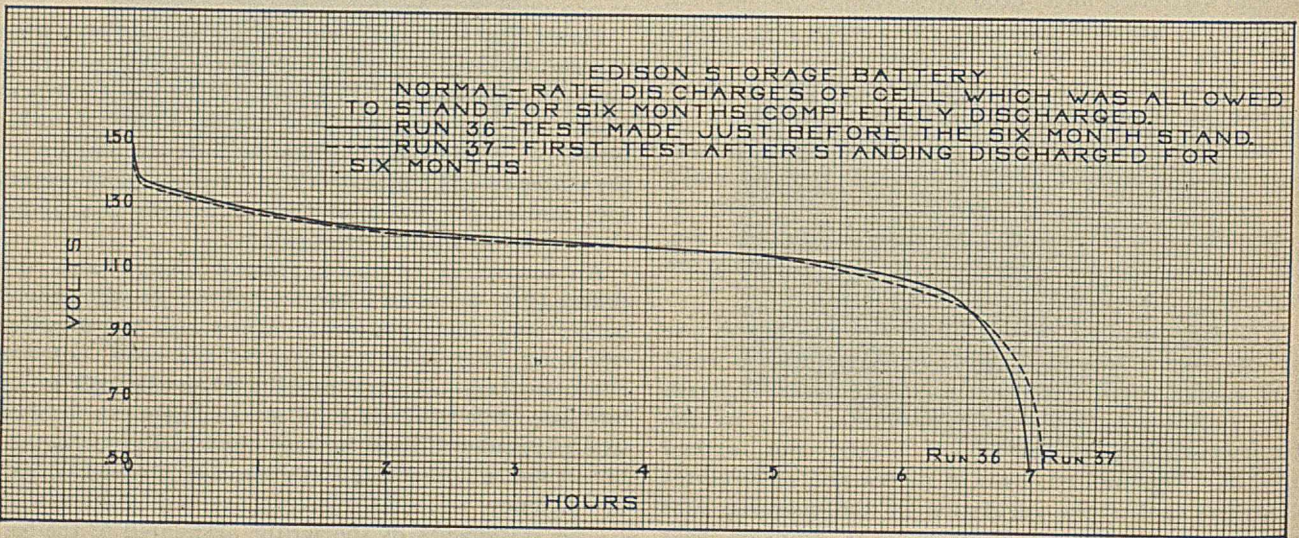

Fig. 7.

cell are based upon fifteen years of experience in use of the cell, while experience with the Edison cell of course does not extend over such a length of time. There is ample proof, however, of its much greater reliability, first in the evidence of the behavior of the battery in commercial use and secondly in the results of laboratory tests.

Efficiency is an exceedingly desirable quality in an energy-storing device, but granted even fair efficiency the availability of the stored energy after one month, six months or a year is a matter of paramount importance. Efficiency means little in economy if the structure of the device is not sturdy. As in the case of investments, a possible high rate of interest cannot be considered with the lower per cent. that can be anticipated with certainty. In relation to the first cost of this battery taken with its permanency, Mr. Edison said in effect that the cost may be considered as an investment, not as a running expense.

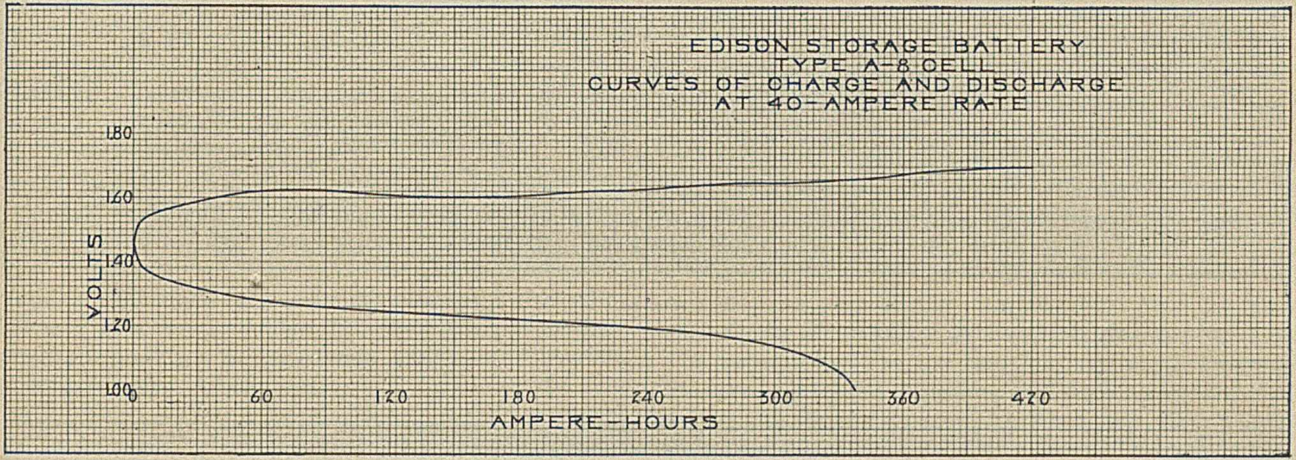

Fig. 8.

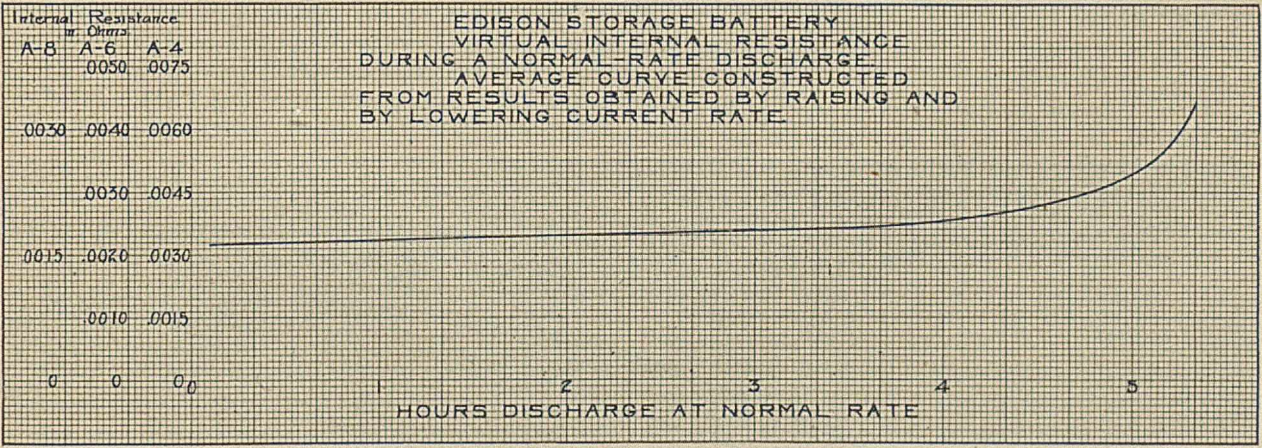

Fig. 9.

The feature of the Edison cell that must appeal to all who use battery current for any purpose is that we have finally in portable form a store of energy that is ready for use at any moment and that may be held indefinitely without material waste. As soon as its merits become generally known it would seem that it would eventually displace every form of battery in present use.

According to the results of trial runs, it would appear that electric pleasure vehicles equipped with Edison cells should no longer be classed as town cars. This statement is made by the Edison Company. "One hundred miles to the charge is quite ordinary, a hundred and fifty miles easy, and runs of over two hundred miles have been made." This, of course, means on a single charge.

An electric vehicle was propelled nearly to the top of Mt. Washington but finally had to turn back on account of a storm. Confirmation of the assertions in regard to dependability of the Edison battery is best furnished by experience of Express Companies, Department Stores, and large retailers who have hundreds of delivery wagons in daily use. The value of this type of energy storage is still better shown by its application to cross-town car propulsion in New York and to omnibuses and drays, a type of service that is most exacting. Two leading Express Companies have in use at the present time one hundred and seventy five delivery wagons equipped with Edison batteries.

The purchaser of an electric vehicle surely need

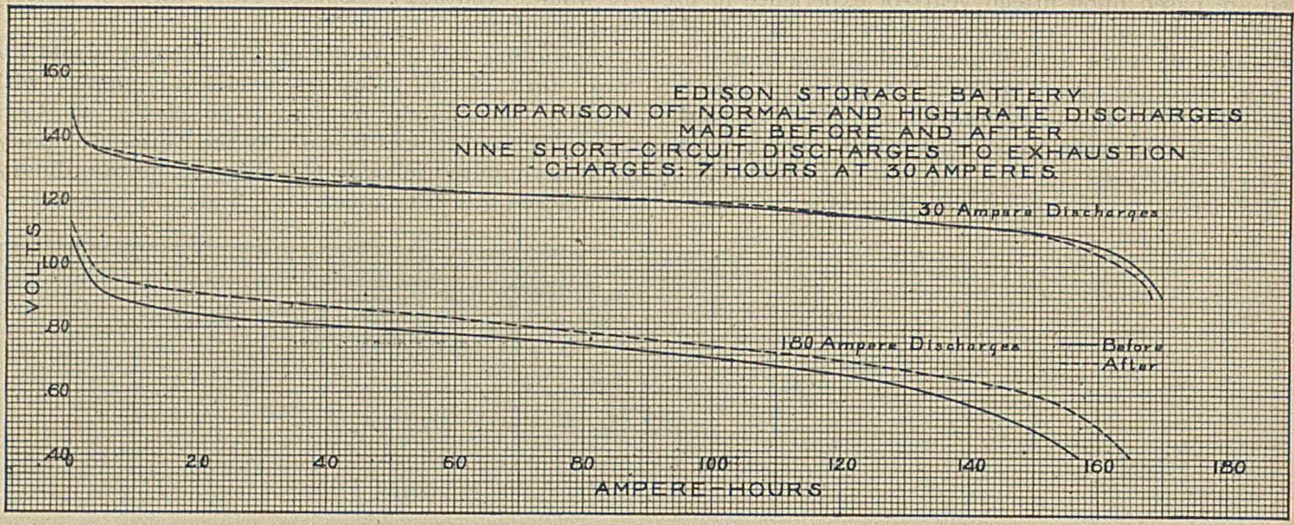

Fig. 10.

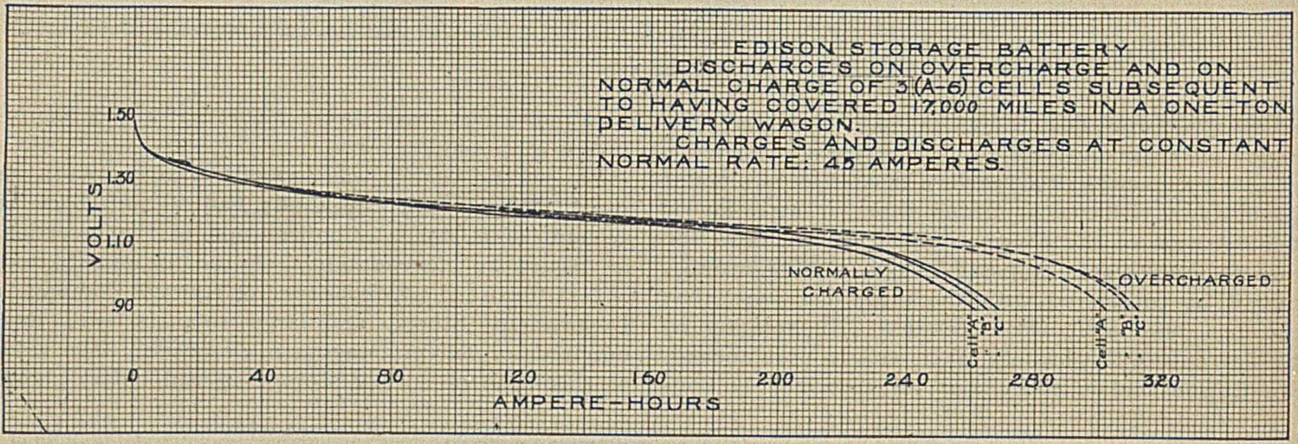

Fig 11.

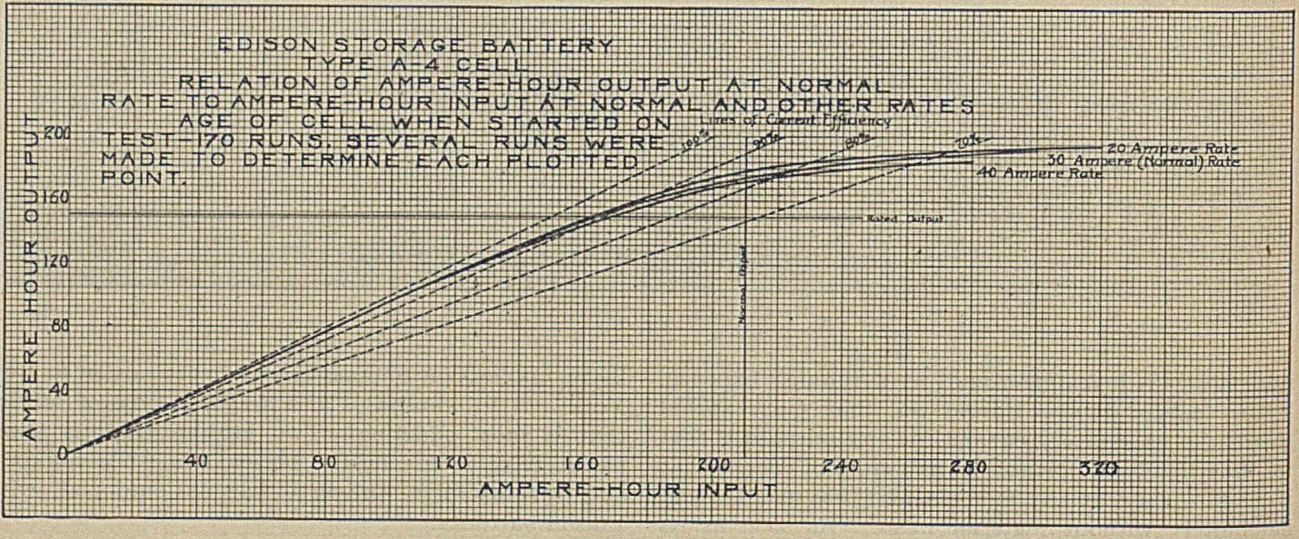

Fig. 12.

not hesitate to purchase an Edison battery, fearing that the battery may not be durable, for one manufacturer of electric vehicles absolutely guarantees to replace anything that goes wrong in the battery up to 50,000 miles of travel.

The history of the method of development of the Edison storage battery is most interesting. In answer to questions of the writer, Mr. Edison stated that all possible chemicals and structure that had been used or could be used for plates and electrolytes were considered at the outset, and cells were made up one by one as knowledge and imagination prompted the selection. Every cell was carefully tested and the behavior recorded. He said: "We had as many as eighteen hundred distinct types of cells on test at one time. We did not construct a few cells and wait a year or two for results, but crowded into the period of observation experience with thousands of cells." Finally he said with emphasis: "An individual's lifetime is far too brief to attain any marked advance in invention unless he extends his experience simultaneously to a very wide range of materials, structures and phenomena. An investigator like Luther Burbank has a great advantage over me for he can carry on millions of experiments at the same time."

The Edison battery is the result practically of the efforts of one man expended almost continuously over a period of eight years and personally directing many thousand experiments which were made. By this I do not mean the battery in a broad and general sense, but I mean the precise mechanical and chemical structure that it now is to-day, and not only that, but practically all machinery and appliances used in its manufacture are the results of Mr. Edison's personal suggestions and supervision. He has had loyal, devoted, and hard-working assistants who have carried out his ideas with enthusiasm, but it is the Edison battery with which we are now dealing, both in fact as well as in name. In the years to come I believe it will be regarded as the greatest monument to his genius, and if the full story of its development were told, I believe it would represent one of the greatest intellectual accomplishments of all time.

AN ELECTRIC HEATER FOR ETHER EXTRACTIONS.

By William H. Ross.

Received September 26, 1911.

Many electrical appliances have been devised for laboratory use, but up to the present illuminating gas, where available, is used as the principal source of heat in most laboratories. This is largely due to the fact that electricity is ordinarily more expensive than gas, and for many purposes not so convenient, since changes in temperature can not be brought about as quickly in an apparatus heated with electricity as with gas. This is true particularly of electrically heated hot plates, or electric heaters for Kjeldahl work.

In the case of electric furnaces, on the other hand, these disadvantages are not so serious. The necessity of bringing about quick changes in temperature is not so important, and as the apparatus may without much inconvenience be surrounded with a very thorough heat insulation, a furnace of this kind may be used very economically. A simple furnace for high temperature work has recently been devised by Benner and may be made with little expense.

In an electric heater for ether extractions the disadvantages already referred to are still less serious. Owing to the low temperature required the expense of heating is immaterial, and a uniform, rather than a variable, temperature is desired. Furthermore, an apparatus of this kind has the advantages of safety and neatness over the gas-heated water bath which is still largely used for this purpose.

The heater herewith described has been in use in this laboratory for some time, and has proved very satisfactory both in the matter of convenience and efficiency.

The outer part of the heater, which is represented in Fig. 1, consists of a rectangular box, 80 × 20 × 12 cm., made of ebonized asbestos, 1 cm. in thickness. The asbestos serves the double purpose of lessening the loss of heat by radiation, and does away with any danger of short-circuiting between the wire system shown in Fig. 2, and the outer box. The box is supported on brass legs, 4 cm. in length.

A galvanized sheet-iron box, B, 74 × 18 × $5^{1}/_{2}$ cm., rests on asbestos supports within the outer box, and at a distance of 2 cm. above the wire system which is supported horizontally on asbestos supports about $2^{1}/_{2}$ cm. above the bottom of the outer box.

The top T of the outer box, which is made of the same material, is detachable from the rest of the apparatus, and has six openings through which the flasks of the extracting apparatus pass, and rest on the bottom of the iron box below. When the current is turned on by means of a switch, S, at the end of the outer box, the flasks not only become heated by contact with the iron support upon which they rest, but are surrounded with a heated atmosphere which minimizes the current required to bring about the extractions. Asbestos covers, C, are provided for the holes which may not be in use. If desired, split covers, SC, may be obtained to fit closely around the necks of the flasks. These are not at all essential, however, as the current necessary to bring about a given rate of extraction is decreased but little by their use.

By means of the regulating switches S_1 and S_2, the current flowing through the apparatus may be varied from 1 to 5 amperes. This is brought about by cutting out the outer strands of wire as the switches are moved from position 1 to position 5. As the strands are strung in the form of spirals, any expansion which takes place on passing the current causes no noticeable lateral displacement of the strands, but simply causes the coils to move a little closer together. Any danger of the strands coming in contact, however, is prevented by separating them with strips of asbestos as shown in Fig. 1.

Brass rods, R, 11 mm. square and 74 cm. long, lie along the sides at the bottom of the outer box

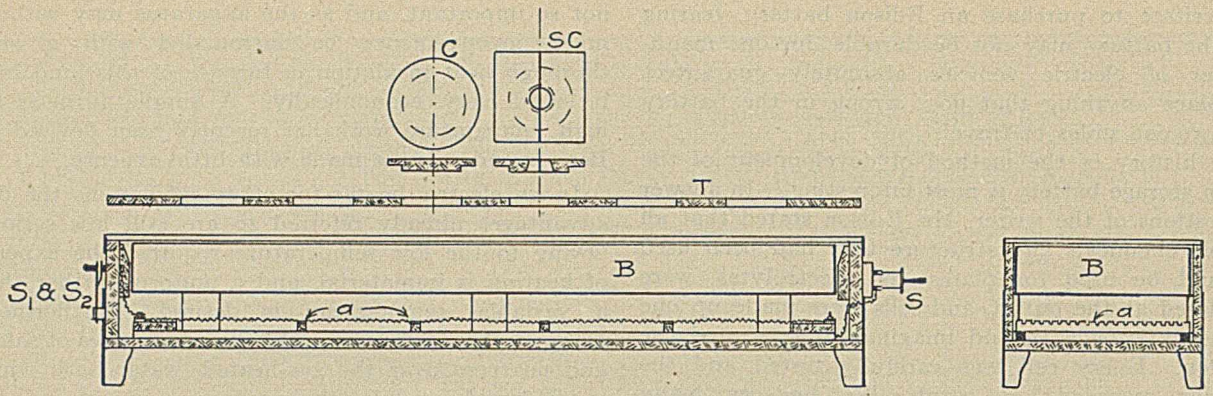

Fig. 1.

and serve the double purpose of giving rigidity to it, and of connecting the electric circuit with the wire system shown in Fig. 2.

Owing to the small current required in making extractions with ether, it was not thought advisable to provide for heating less than six flasks at a time. The resistance wire is made of No. 22 nichrome alloy which affords a resistance of 0.937 ohm to the foot.

When the apparatus is connected with the 110-volt circuit, the strength of current obtained and the length of wire through which the current passes at each step as the switches are moved from position 1 to position 5 are as follows:

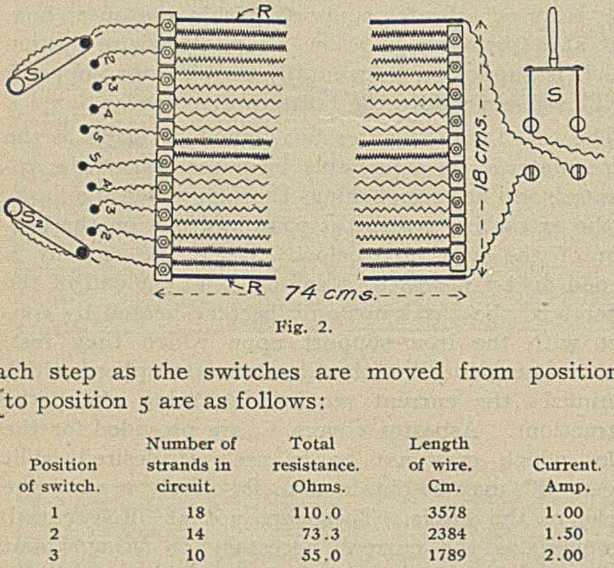

Fig. 2.

Position of switch.	Number of strands in circuit.	Total resistance. Ohms.	Length of wire. Cm.	Current. Amp.
1	18	110.0	3578	1.00
2	14	73.3	2384	1.50
3	10	55.0	1789	2.00
4	6	40.0	1301	2.75
5	2	27.5	895	4.00

By changing the switches one at a time, twice the number of steps in the variation of the current may be obtained.

The inner vessel is water-tight and may be used as a liquid bath if desired. When used as a water bath with the top plate removed, the water becomes heated to a temperature of about 42° with the switches in position 1. This causes the ether to distil at almost exactly the same rate as when the apparatus is used as an air bath with plate P in place. When it is desired to heat more than six flasks at a time, this can be conveniently done by removing the top plate, in which case the apparatus can be more economically used as a water bath.

The minimum temperature obtained with the top plate removed and glycerine in the inner box is 60°. This increases to 80° with the plate in place, while with the switches in position 5 a maximum temperature of 135° may be obtained.

The apparatus as thus described may be obtained from the Central Scientific Co. at a very moderate cost.

The advantages of the apparatus may be stated as follows:

(1) The flasks rest on a hot metallic plate, and are surrounded by a heated atmosphere in consequence of which a very low current is sufficient for extractions with ether.

(2) The temperature of the apparatus is capable of being changed between considerable limits which enables the same apparatus to be used for making extractions not only with ether, but also with acetone, chloroform, carbon tetrachloride, and other solvents commonly used in making extractions. The same feature enables the apparatus to be heated up quickly at first then used for making extractions with ether.

(3) After the extraction is complete, the solvent may be evaporated from the flasks without danger of ignition by replacing them in the apparatus and turning on a low current.

(4) With the top plate removed the apparatus may be used as a hot plate for making slow evaporations, and for other purposes.

(5) If so desired it may be used as a liquid bath by placing water, or some other high boiling-point liquid, in the inner box.

Agr. Expt. Station,
University of Arizona,
Tucson.

TWO NEW PIECES OF CHEMICAL APPARATUS.

I. Apparatus for the continuous extraction of liquids with immiscible solvents lighter than water.

II. Apparatus for quantitative reactions which depend on the measurement of an evolved gas.

By R. F. Bacon and P. B. Dunbar.

Received September 26, 1911.

I. CONTINUOUS LIQUID EXTRACTOR.

This apparatus was designed originally for use in the extraction of lactic acid from ketchup and other fruit products. Its principal advantages are compactness, the elimination of ground joints and stoppers, and practically complete condensation. Seven of the extractors may easily be placed side by side on a 24-inch hot plate. They have been made for the authors at a cost of $1.50 each, but may be constructed in the laboratory by any one having ordinary skill in glass-blowing.

The apparatus consists of four parts: (1) A jacket flask; (2) an extraction thimble; (3) an ordinary Gooch funnel; (4) a condenser.

(1) The jacket flask (Fig. 1) A is made of glass tubing 2 inches in diameter and approximately one-sixteenth of an inch thick; it is 20.5 inches long and is enlarged to a diameter of about 3 inches at its lower or sealed end, as shown in the illustration. (2) The extraction thimble (Fig. 1) B is an ordinary test tube having a diameter of 1.5 inches and a capacity of 100 cc. when filled to within 1.5 inches of the top. One-fourth of an inch from its top and on opposite sides of the tube are placed two holes about one-fourth inch in diameter. (3) The Gooch crucible funnel is (Fig. 1) C; those used in this laboratory are 8.5 inches long. When dense liquids are to be extracted it is sometimes necessary to increase the length of the funnel. The lower end of the stem is ground at an angle of 45 degrees. (4) The condenser (Fig. 1) D is designed to hang loosely in the jacket flask. Its details are evident from the drawing. A simpler form of condenser, which is just as efficient, may be made by sealing one end of a $1^3/_4$-inch tube and drawing it to a point. The open end is flared somewhat to permit the tube to hang in the jacket. The condenser is closed by a two-holed rubber stopper, through which pass the inflow and outflow tubes.

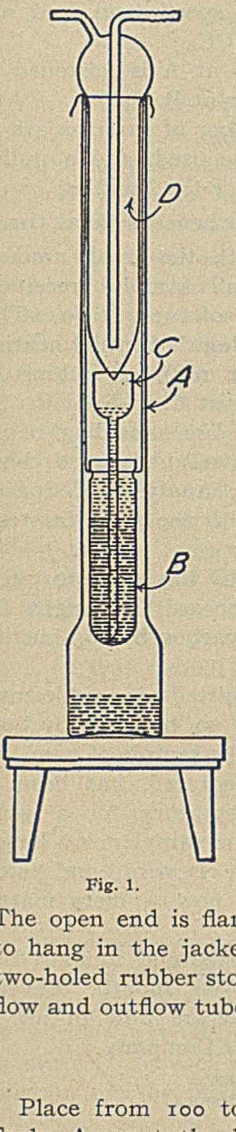

Fig. 1.

OPERATION.

Place from 100 to 150 cc. of ether in the jacket flask A; put the liquid to be extracted (100 cc.) in the test tube B, insert the funnel in the same tube and suspend it in the jacket flask, about 3 inches above the bottom, with a copper wire which passes through the holes in the test tube and is hooked over the rim of the jacket flask. Insert the condenser in the top of the jacket flask. The condensation is usually so perfect that no ether vapors escape into the room. The condensed ether drops from the point of the condenser into the funnel and is carried to the bottom of the test tube whence it flows up through the liquid and overflows at the top.

The efficiency of the extractor may be increased by the use of a glass spiral attached to the stem of the Gooch funnel, as described by Kempf.[1]

II. APPARATUS FOR THE MEASUREMENT OF AN EVOLVED GAS.

The apparatus represented in Fig. 2 was devised to give in a compact and easily manipulated form an apparatus which will allow of the measurement of an evolved gas without first sweeping out all air or other indifferent gases. It consists of a graduated funnel tube, A, a reaction chamber, B, an absorption tube, C, filled with glass beads, a eudiometer, D, and a leveling tube, E. A heating coil may be wrapped around the reaction chamber B when desired. The absorption tube C, which is sealed onto the eudiometer, fits into the reaction chamber B by means of a ground joint at F.

The manner of using the apparatus may best be illustrated by one of the reactions which can be advantageously carried out in it. Spica[2] estimates citric acid from the carbon monoxid evolved by decomposing this acid with strong sulphuric acid at 100° C. He runs air-free carbon dioxid through a flask containing the citric acid until all air is displaced from the apparatus. He then adds concentrated sulphuric acid, heats to 100° C., drives over the evolved carbon monoxid with a stream of air-free carbon dioxid, and collects the gas in a eudiometer over a sodium hydrate solution. The method as carried out by him is accurate, but requires considerable care and attention to remove the air from the apparatus completely, to insure that all evolved carbon monoxid is swept over into the eudiometer, and to prevent the strong sodium hydrate solution from sucking back into the reaction flask containing carbon dioxid and sulphuric acid. In the apparatus proposed by us no attempt is made to remove the air before reaction, the volume of evolved gas being simply measured by the increase in volume of the total gases after reaction. Thus the Spica method as carried out in this apparatus is as follows:

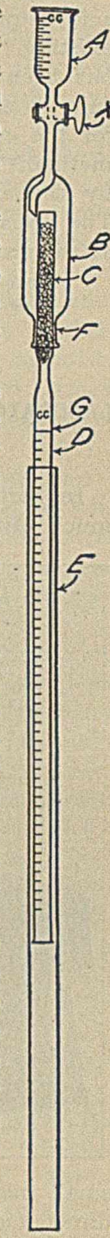

Fig. 2.

Place about 0.2 gram of citric acid in the reaction chamber B, open the stopcock X and bring the liquid (in this case a strong sodium hydrate solution) to the zero mark G in the eudiometer tube by raising or lowering the leveling tube E. The air in the apparatus is then at atmospheric pressure. Close X. To A add about 15 cc. of concentrated sulphuric acid. Lower the leveling tube so that the air in the apparatus is under reduced pressure. By carefully opening the stopcock X run in exactly

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[1] *Chem. Ztg.*, **34**, 1365 (1910); *C. A.*, **5**, 1350 (1911).

[2] *Chem. Ztg.*, **34**, 1141 (1910).

10 cc. of the sulphuric acid. Close X and heat to about 100° C. by means of the heating coil until the reaction is complete. Let the apparatus stand until the absorption of other gases (sulphur dioxide, etc.) is complete and it has reached room temperature. Bring the gas in the apparatus to atmospheric pressure by means of the leveling tube E. The gas reading in the eudiometer minus 10 cc. (for the added sulphuric acid) equals the volume of the evolved gas at the existing temperature and pressure. The apparatus has been used in this laboratory with accurate results to estimate citric acid by the Spica method and for the estimation of amino acids by the Van Slyke method,[1] which depends on the evolution of nitrogen, by the action of nitrous acid on the amino acids. The apparatus is readily cleaned by taking it apart at the ground joint F.

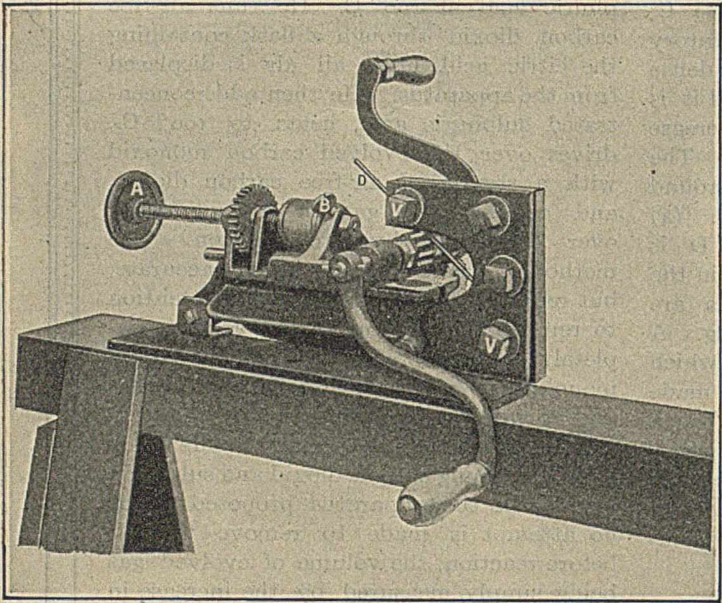
Bureau of Chemistry,
Washington, D. C.

LABORATORY MILLING MACHINE FOR SAMPLING STEEL.

By Chas. Morris Johnson.

Received November 1, 1911.

In certain kinds of steel the writer encountered much difficulty in getting samples of sufficiently small mesh for the determination of carbon by the direct method described by him several years ago. ("The Chemical Analysis of Special Steels"—John Wiley & Sons, 1909.)



The trouble was confined to thin sheets, wire, hack saw steel, band saw steel, razor blades, resistance ribbon, nails and small samples of all kinds that are irregular in shape and difficult to hold in the drill press vise.

The machine shown in the illustration afforded a successful means of avoiding various time-consuming expedients.

The sample D of wire, for example, is held in the vise V-V. The millings are taken up by means of a cutter, made of the best high-speed steel, and are caught on a piece of cardboard at C.

The automatic feeding device at A is hastened in its action by tightening the screw at B.

If desired, where a large number of samples are to be milled, a small motor can be used, and a pulley can be attached instead of one of the handles.

The milling cutters can be sharpened several times.

It is desirable, and well worth the small amount of time involved, to anneal all samples received, if they are not already in a softened state. This operation can be done in a half hour's time by heating the sample to 800° C. (bright red), quenching at once in water and then holding at 620°–630° C., for 20 minutes (low red). The annealing of 13 per cent. manganese steels has also been previously described in "Analysis of Special Steels, etc." together with the chemical tests for perfect annealing.

The millings obtained by this laboratory tool are not sifted, as they are just right for direct determination of carbon by combustion in oxygen.

If the sample submitted is sufficiently rigid, it does not need to be held by both ends, as in the case of the sample of wire.

This machine, as illustrated, has been in use in the writer's laboratory for a year. Since its introduction, the samplers no longer dread the appearance of wire and steel ribbon, this work being now a mere matter of easy routine.

The first cost was a bagatelle compared to the saving of labor in one month. Several copies of this milling tool are now in use in other laboratories of this Company.

Laboratory of Park Works,
Crucible Steel Company of America,
Pittsburgh.

ADDRESSES.

RECENT DEVELOPMENTS IN BAKELITE.[2]

By L. H. Baekeland.

Received November, 13, 1911.

My subject involves the use of two main raw materials, phenol or carbolic acid, which is found in gas tar, and formaldehyde. The latter is now manufactured by the oxidation of wood-alcohol.

I should state that the name of formaldehyde is used in a rather broad sense. I never have seen real formaldehyde, CH_2O, and very few chemists have had occasion to examine it. It is a gas which can be made to liquefy and solidify by the intense arti-

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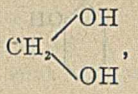
[1] *Ber. d. chem. Ges.*, [3] **43**, 3170 (1910).

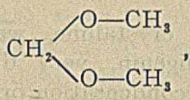
[2] Read at joint meeting of New England Section, Amer. Chem. Soc. and Soc. Chem. Industry, Boston, Nov. 10, 1911.

ficial cold attainable by means of liquid air.[1] Solidified CH_2O melts at —92° C. The commercial product, designated ordinarily under the name of formaldehyde, is a watery solution of formaldehyde, containing at the same time variable proportions of methylalcohol. In these solutions, formaldehyde is present partially as methylenglycol,



$$\mathrm{CH_2}\begin{array}{l}\diagup\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array},$$

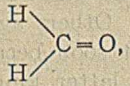
and as methylal,



$$\mathrm{CH_2}\begin{array}{l}\diagup\mathrm{O—CH_3}\\ \diagdown\mathrm{O—CH_3}\end{array},$$

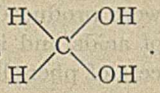
accompanied with variable amounts of several distinct polymers of formaldehyde, of polymers of methylenglycol, or polymers of partial anhydrides of methylenglycol, more or less directly related to paraform, trioxymethylen and similar substances.

The thermochemical researches of Delepine[2] had already shown, in watery solutions, the existence of stable hydrates, which are not decomposed by distillation, and the later work of Auerbach[3] leave no further doubt on the very complicated composition of so-called formaldehyde solutions. The latter are merely mixtures of various chemical compounds which ultimately react in the same way as CH_2O, and which, for practical purposes, are equivalents for each other in the chemical reactions where formaldehyde or methylen-compounds are used. The main point in all these reactions is that the group methylen $=CH_2$ should exist in a mobile condition. It matters little whether this group $=CH_2$ presents itself as true formaldehyde or oxymethylen,



$$\begin{array}{r}\mathrm{H}\diagdown\\ \mathrm{H}\diagup\end{array}\mathrm{C=O},$$

or as its hydrate as methylenglycol,

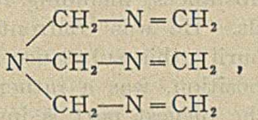


$$\begin{array}{r}\mathrm{H}\diagdown\\ \mathrm{H}\diagup\end{array}\mathrm{C}\begin{array}{l}\diagup\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array}.$$

The same remark applies to its polymers, paraform, trioxymethylene, or other polymers of formaldehyde, or polymers of methylenglycol, or partial anhydrides thereof. All these substances can be substituted for each other, and the final result of the reaction can be made practically the same.

So well was this known that the early work of Ad. Baeyer and his pupils on condensation products of phenols and formaldehyde was carried out by means of the latter's methylen representatives: methylal, methylenacetate, methylenchlorid, or methyleniodid, for the simple reason that commercial formaldehyde was unavailable at that time.

Ammonia combines very easily with formaldehyde and forms hexamethylentetramin,[1]



$$\mathrm{N}\begin{array}{l}\diagup\mathrm{CH_2—N=CH_2}\\ —\mathrm{CH_2—N=CH_2}\\ \diagdown\mathrm{CH_2—N=CH_2}\end{array},$$

So eager is the tendency of combining with ammonia, that if formaldehyde, or any of its equivalent compounds, which keep the group CH_2 in mobile condition, is put in presence of an ammonium salt, like ammoniumchlorid, acid is expelled, and hexamethylentetramin is formed.[2]

Consequently, whenever an excess of formaldehyde or a formaldehyde compound is put in presence of ammonia or an ammonium salt, hexamethylentetramin is formed forthwith, so that mixtures of ammonia and formaldehyde, or hexamethylentetramin, are practically the same thing. On the other hand, hexamethylentetramin, in presence of acids, reliberates easily formaldehyde. There is nothing astonishing that in the condensation of phenols and formaldehyde we should be able to replace formaldehyde by other related compounds.

Let it then be understood that in the reaction I am about to explain, whenever I refer to formaldehyde, this broad denomination includes many substances which are practically equivalent in their chemical action to the orthodox, but elusive true formaldehyde, CH_2O.

When phenol is acted upon by means of formaldehyde, or its equivalents, a most varied set of reactions can occur; even by starting from the same raw materials, new substances may be produced which, according to conditions of operation, may vary considerably in appearance, as well as in chemical and physical properties.

The earlier investigators, like Ad. Baeyer and others,[3] were especially on the lookout for substances of definite chemical constitution, which could be easily isolated, crystallized and purified for the development of their purely scientific work; if they obtained non-crystalline bodies, of resinous appearance, this was merely considered as a drawback, and constituted an unpleasant obstacle in their theoretical research work. Their resins did not seem to attract much of their attention, and the study of the resinous products was soon abandoned in favor of the crystalline bodies which could be obtained. Under the circumstances, it is quite natural that no special effort had been made to produce these resinous bodies, under such conditions that they could be used for definite technical purposes.

When in 1891 formaldehyde had become a relatively inexpensive article of commerce, Kleeberg[4] took up this matter anew, and found that by bringing together a mixture of formaldehyde solution, phenol and hydrochloric acid, a violent reaction ensues,

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[1] Raikov, *Chem. Ztg.*, **26**, 135; **12**; **11** (1901). Kekule, *Ber.*, **25**, 2435. Harries, *Ber.*, **34**, 635.

[2] *Compt. rend.*, **124**, 1454; *Bull. soc. chim.*, **17**, 849.

[3] F. Auerbach, also Auerbach and Barschall, *Arb. kais. Gesundh.*, Band XXII, Heft 3 and Band XXVII, Heft 1, Verlag Julius Springer, Berlin.

[1] See Wohl, *Ber.*, **19**, 1892. Tollens, *Ber.*, **17**, 653. Carl Goldschmidt; page 29. Bonn, Verlag von Friedrich Cohn, 1903.

[2] See Cambier, Brochet, *Compt. rend.*, **120**, 557.

[3] *Ber.*, **5**, 1095; **19**, 3004 and 3009; **25**, 3477; **27**, 2411.

[4] *Ann.*, **263**, 283.

and the whole mass changes to an amorphous, hard, resinous body, of irregular shape, a mixture of various heterogeneous substances, including remnants of the reacting materials. He was confronted by the fact that trying to purify this substance, or to establish a constant composition, was a rather thankless job, especially so as the biggest part is insoluble and not amenable to the usual methods of purification; after giving a limited attention to this subject, he pursued his work along the line of other condensation products, which can be obtained in crystalline form.

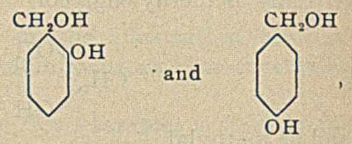
Afterwards, various attempts were made by Smith, Luft, Blumer, Story, DeLaire and others, to try to modify this reaction, so as to produce more definite bodies than those obtained by Kleeberg.[1] Their efforts were directed towards moderating the reaction by limiting the temperatures, or by diluting the reacting materials in suitable solvents. It was thus found that, according to circumstances, resins could be obtained which are soluble in alcohol and similar solvents, and which can be heated and melted, and which under treatment of heat remain indefinitely fusible, and behave much like shellac or similar natural resins. For that reason, they are called shellac-substitutes, and I have published a special paper on this subject,[2] in which I designate these artificial soluble and fusible resins, under the general name of Novolak.

Under other conditions, entirely different bodies are obtained which, although resinous in appearance, can no longer be considered as true resins, and lack the chemical characteristics of resins. They are infusible and insoluble. However, the preparation of these infusible substances involved several objectionable conditions, which made them of little, if any, practical value. All this is described in my former publications on this subject.[3]

I undertook a systematic study to establish the chemical constitution and the relation which exists between these infusible bodies, the fusible, soluble, resinous condensation products, and the substances from which they are derived. I was able to dissect this perplexing reaction in several distinct transition stages, which can be produced at will. It seemed at first that the formation of these very dissembling bodies was simply a matter of relative proportions of reacting materials, or of quantity of condensing agents, but I became convinced that this is not so simple and that the reaction involved several, until then unobserved or neglected, phenomena which have a paramount bearing on the results.

By conducting the process in several stages, and more particularly by effecting the synthesis from different starting points, I succeeded in gaining enough insight into the problem that I could devise some sure practical methods for obtaining new results. Since then, several years of uninterrupted hard work have enabled me to devise various technical applications, with most of which you are already acquainted. One of my first problems was to determine why different experimenters had obtained such dissimilar results when starting from almost identical products. For instance, Lederer[1] and Manasse[2] by acting with one molecule of CH_2O on one molecule of C_6H_5OH, in presence of one molecule of NaOH, then acidulating, obtained ortho- and paraoxybenzylalcohol,

$C_6H_5OH + CH_2O = H_2O +$



which is a nicely crystalline, water-soluble body, known also as saligenin, very different from the resinous amorphous condensation products. Saligenin had formerly been prepared from its glucoside, salicin, which was extracted from the willow tree.

Then again, DeLaire,[3] operating under rather similar conditions, using about the same proportions of alkali, phenol and formaldehyde, then acidulating, and heating afterwards, obtained fusible soluble resins of totally different character than oxybenzylalcohol. These resins are identical with the soluble fusible resins which he and others obtained by heating directly acids with a mixture of formaldehyde and phenols, but they are totally different from the infusible, insoluble mass Kleeberg and others obtained by heating hydrochloric acid with the same mixture of phenol and formaldehyde. At that time, those results seemed rather irreconcilable with each other, and it very often happened that two operators, starting from the same mixtures, obtained totally different products by simply changing somewhat their way of working. Some workers in this line seemed to pin their faith to the fusible, soluble resins, or Novolak, and used every means to exclude the disturbing insoluble bodies which tended to form. Others again tried to utilize the infusible bodies. It soon became evident to me that the bodies of the latter kind prepared up till then had not attained their full best qualities because they were produced at too low a temperature in presence of acids and in admixture with solvents or with an excess of phenol.

I found that decidedly higher temperatures than those preconised for these products were very desirable, not only for improving the end product but more especially for insuring rapid formation and rapid molding. But when I tried to employ high temperatures, I was immediately confronted, like my predecessors, with the same difficulties; namely, high temperatures bring about violent uncontrollable reactions, accompanied with self-heating and with the evolution of gaseous products, which render the mass porous. This was the very reason why those who had preceded me had carefully recommended in all their descriptions, not to use temperatures exceeding 50 to 80° C., or at the utmost, 100° C.; even then, they were compelled to use solvents or,

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[1] See Baekeland, This Journal, **1**, No. 3, March, 1909, published by the American Chemical Society, Easton, Pa.

[2] See Baekeland, This Journal, **1**, No. 8, August, 1909.

[3] See Baekeland, *Ibid.*, **1**, No. 3, March, 1909, **1**, No. 8, August, 1909.

[1] *J. prakt. Chem.*, [2] **50**, 224.

[2] *Ber.*, **1984**, 2409–11; D. R. P., Baeyer, 85,588; U. S. P., Manasse, 526,786, 1894.

[3] French Patent, No. 361,539.

in some cases, an excess of phenolic body so as to moderate the reaction by these diluents.

I became aware of the fact that the disturbing emission of gaseous products, whenever the reaction is carried out at too high a temperature, has the characteristics of chemical dissociation. Its disturbing action could be moderated by introducing a solvent, for instance, an excess of phenol, in which the gaseous products could provisionally accumulate until they established a dissociation equilibrium. But I concluded that the easiest and most practical way to prevent gaseous dissociation, and the resulting porosity of the mass, was to exert a suitable counterpressure. This allows us to use as high a temperature as we may desire, by increasing the counterpressure accordingly. This can be done in several ways, either by heating in a closed vessel in which the pressure raises by itself, or better in a vessel in which air or another gas is pumped, under pressure, before the heating begins. One of the most practical ways, and specially suitable for molding, is the use of a heated hydraulic press.

Permit me to say here that before I took up this subject, no other methods for molding infusible condensation products of phenols and formaldehyde had been suggested than so-called cast-molding, consisting in pouring the original mass in a mold and heating moderately without pressure until solidification sets in.

The technical problem was advanced further by utilizing the following observation:

If formaldehyde and phenols are heated in presence of an acid condensing agent, an insoluble body *may or may not* be the result. This does not depend on the amount of acid nor whether the reaction is allowed to proceed violently, or slowly; neither does it depend on the amount of formaldehyde which has been used; but it all depends on the amount of formaldehyde which has really entered into reaction. For instance, if the reaction be carried out in presence of an acid condensing agent, with an amount of phenol exceeding 15 molecules of phenol for 14 molecules of formaldehyde, a fusible, soluble resin of the Novolak type is most likely to form. The same thing occurs even if large amounts of formaldehyde are used, but if for some reason or another, enough formaldehyde is volatilized, or otherwise lost during the reaction.

I found that these uncertainties do not exist if, instead of an acid condensing agent, we use a small amount of a base. Bases had been used before but in much larger proportions, by which they form substances entirely different from those I have in view. Relatively small amounts of ammonia, alkalies, amines or other basic substances, added to a mixture of phenols and formaldehyde, enabled me in every case, after heating, to produce insoluble, infusible end products, regardless whether the amount of phenol is or is not in excess. With the use of small amounts of basic condensing agents, there is no longer any doubt as to the result, and the reaction becomes so easy to control as to lend itself to the most varied industrial applications. By the use of bases the initial reaction can easily be interrupted at will, so as to obtain stable intermediate products, which simplify the whole process so as to make it a practical industrial operation. Furthermore, the presence of these small quantities of bases in the initial condensation product accelerates, at relatively low temperatures, the final hardening by polymerization. This beneficial accelerating action is so pronounced that, with some precautions, the process of hardening can be carried out in a much shorter time, and without the use of any counterpressure; for instance, by starting at relatively moderate temperatures, say about 80° C., and as soon as the mass begins to harden by raising the temperature with increasing rapidity to 110° C. and over. For very thin layers, this precaution of gradual heating can even be omitted, and the maximum temperature can be applied at once, without any danger of blisters or porosity.

However, in most cases it is decidedly more practical to heat directly at maximum temperature, under suitably increased pressure. In this way, hardening and moulding can be accomplished in as short a time as one to five minutes, according to the thickness or the size of the object. My published patents contain a description of these processes, and I shall limit myself to the following brief description:

About molecular proportions of phenol and formaldehyde are boiled in presence of suitable amounts of ammonia, or sodium hydroxide. This gives an initial product which is called A, and which can be purchased in the trade either in liquid, or in solid condition. A is the immediate and first result of the condensation reaction, whereby formaldehyde in reacting upon phenol increases the carbon nucleus of its molecule, this phenomenon being accompanied by a corresponding chemical elimination of water. This A, our initial condensation product, is soluble in alcohol, acetone and similar solvents. Certain varieties of A can be kept indefinitely, or at least for a long time, without alteration. A is characterized by the very distinct property that when it is further heated, it will ultimately be transformed into a final infusible, insoluble substance, of great hardness, called Bakelite "C," and this is the final product at which we aim in the whole process.

Solid A, on account of its physical appearance and its solubility in alcohol or acetone, might easily be mistaken for one of the permanently fusible, soluble resins of the Novolak type. But such a mistake is impossible if we bear in mind that Solid A, when heated, although it may melt for awhile, soon becomes hard, infusible and insoluble by polymerization. Novolak, on the contrary, if heated, simply melts and sets again by cooling, but it does not harden to an infusible, insoluble body by simple application of heat.

In my former publications[1] I have described also an intermediate product, B, the existence of which is of considerable importance for certain industrial

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[1] Baekeland, *loc. cit.*

applications, because, although being infusible and insoluble, it nevertheless, possesses the property of softening if heated, and of welding and molding under the combined action of heat and pressure.

There are several other ways of obtaining "C," for instance, Lebach (Knoll & Co.) uses a base as a condensing agent, and mixes the so obtained "A" with a strong acid, and heats at a moderate temperature.[1]

"C" can also be produced by heating oxybenzyl alcohol with CH_2O, or its equivalents.[2] Or instead of starting from oxybenzyl alcohol, we may start from Novolak, and heat it with CH_2O, or equivalent substances.[3] DeLaire[4] has already shown that the fusible soluble resins are anhydrides of phenol alcohols. This can easily be demonstrated by heating, preferably *in vacuo*, oxybenzyl alcohol in a test tube at 160-170° C. Heating oxybenzyl alcohol, in presence of acid solutions, favorizes considerably the formation of these anhydrides, or saliretins, saligenosaligenin, and similar products.[5] I believe this explains to us why bodies of the Novolak type are more easily engendered in presence of acid condensing agents, provided the CH_2O be not used in excess.

The intervention of condensing agents for the formation of fusible, soluble resins of the Novolak type is not indispensable. This has been shown as far back as 1905 by Story,[6] who, by simply boiling an excess of phenol with formaldehyde *without any condensing agent*, and evaporating afterwards, has obtained a soluble, fusible resin of the Novolak type. Lately, Aylsworth[7] has confirmed this method in a somewhat more complicated way. All these fusible resins are simply anhydrides of the corresponding phenol alcohols. Their fusibility and solubility are augmented by the presence of small amounts of phenolic bodies. In my former publication "On Fusible, Soluble Resinous Condensation Products of Phenols and Formaldehyde,"[8] I considered these bodies as definite compounds of saliretin products, with a small excess of phenol. More recent work on the same subject, the details of which are not yet ready for publication, compels me to abandon this interpretation. We have to deal here simply with physical mixtures in the form of colloidal solid solutions of saliretin products with very small quantities of phenols. These small amounts of phenol are retained stubbornly by the phenol alcohol anhydrides or saliretin products forming therewith a solid solution; this accounts for the difficulty of their complete removal.

This makes the chemistry of this whole subject extremely simple. The fusible, soluble resins of the Novolak type are merely the old known saligeno saligenins, saliretins, or anhydrides of phenol alcohols, containing in some cases, in solid solution, a smaller or larger amount of phenols.

If then we take into consideration that I succeeded in making C by heating six molecules of oxybenzyl alcohol with at least one molecule CH_2O or its equivalent, and that the same result is attained by heating Novolak or other anhydrides of phenol alcohols with the requied amount of formaldehyde, the explanation of a heretofore rather perplexing set of reactions becomes exceedingly simple.

Instead of directly preparing Solid A by starting with phenol and formaldehyde and a base, we can make it in two steps: first, prepare Novolak or any other saliretin products and then melt and mix it with the polymers of formaldehyde, and thus obtain a variety of Solid A, practically identical to the Solid A obtained by direct action of phenol and formaldehyde in presence of a base. This Solid A, by further action of heat, will then change into hard infusible, insoluble "C."

The similarity of the Solid A thus prepared is even greater if, instead of using formaldehyde, we use a mixture of formaldehyde and ammonia, so as to accelerate the hardening process. In place of this mixture of formaldehyde and ammonia, we can use its preformed and direct equivalent, hexamethylentetramin. However, in the latter case the amount of ammonia introduced into the mixture, with the required amounts of CH_2 group, becomes much larger than strictly necessary, and on account of this as soon as the final hardening sets in this excess of ammonia is liberated.

If the temperature of such a hexamethylentetramin mixture be raised above 110° C., self-heating starts in, and the whole mass raises like a sponge, while hardening: this on account of the sudden liberation of ammonia vapors. This phenomenon which I show you here is in direct contradiction with the statement of Mr. Aylsworth.[1] It is quite true that my method of using counterpressure in a hydraulic press, or otherwise, can easily be called into service here, so as to allow the use of the high temperature at which rapid molding and hardening becomes possible. In this respect, small amounts of fixed alkalies, like caustic soda, have decided advantages over ammonia, or hexamethylentetramin, in as far as they do not exaggerate the tendency of forming gaseous products by the elimination of NH_3, which causes foaming and porosity during the application of heat in the hardening process.

The properties of Bakelite, its chemical constitution, and some of its industrial applications, have been so often described that I will dispense with a general repetition thereof. The fact that it only chars at relatively high temperatures, its infusibility, its hardness, and tenacity, its resistance to physical and to most chemical agents, and its ease of manipulation explain sufficiently its uses in the arts.

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[1] See U. S. P., Lebach, 965,823.

[2] See Baekeland, THIS JOURNAL, **1**, No. 3, March, 1909.

[3] See Baekeland, "On Soluble, Fusible, Resinous Condensation Products of Phenols and Formaldehyde," THIS JOURNAL, **1**, No. 8, Aug., 1909; Belgian Pat., 213,576, February 15, 1909.

[4] See British Patent, 15,517, 1905.

[5] Beilstein, *Organ. Chemie*, **2**, 1109 (1896). R. Piria, *Ann. Chem.*, **48**, 75; **56**, 37; **81**, 245; **96**, 357. *Moitessier Jahresbericht*, **1886**, 676; K. Kraut, *Ann. Chem.*, **156**, 123. Gerhardt, *Ann. Chim. Phys.*, [3] **7**, 215. F. Beilstein and F. Seelheim, *Ann. Chem.*, **117**, 83. C. Schotten, *Ber.*, **1878**, 784.

[6] D. R. P., 308,449.

[7] Belgian Patent, 232,899.

[8] THIS JOURNAL, **1**, No. 8, August, 1909.

[1] See Belgian Patent, Aylsworth, 232,899, February 11, 1910.

In my former publication on the subject, I have insisted, in order to better differentiate its properties from those of hard rubber and celluloid, that it lacks the flexibility of the two latter products, but I have found since then that my statements have been taken too absolutely, instead of in a comparative sense. Here is, for instance, a thin plate of Bakelite, which is flexible enough for many purposes, and which is, furthermore, quite strong, but you will notice that if I bend it in an exaggerated manner it suddenly will snap off and break in many small pieces. It resembles in this respect a thin plate of glass, but it is not so fragile and is more flexible. Thrown on a hard surface, it will not break as easily as glass and will rebound. Nevertheless, it cannot stand the seemingly endless bending of the very flexible varieties of celluloid. There is no difficulty whatever, by the introduction of some substances which produce colloidal solid solutions, to make Bakelite so soft and flexible that a rod thereof can be twisted around one's finger; but in introducing these extra matters, many of the other excellent qualities of Bakelite are sacrificed to a considerable extent; for those applications where great flexibility is required, rubber and celluloid answer, incomparably better, the purpose.

I found that we can enormously increase the practical uses of Bakelite by incorporating it with structural fillers, like fibrous or cellular bodies. The beneficial action of the latter is remarkable, and seems to consist mainly in modifying the shattering wave which develops whenever an object made of Bakelite is submitted to a violent shock. Some substances, like rubber or celluloid, are weakened if they are mixed with large amounts of fibrous materials. But Bakelite is strengthened by fibrous materials, on account of its low flexibility and other specific properties, probably also by the fact that its fusible parent "A" impregnates homogeneously any fibrous or cellular materials with which it is incorporated, instead of remaining on the surface like rubber or celluloid. It produces, with fibrous fillers compositions which are strikingly much stronger and less breakable than if it be used alone or in conjunction with structureless fillers. This valuable property has been put to excellent advantage in the manufacture of many molded and impregnated articles where Bakelite is used in smaller proportions as a binder for fibrous bodies. This is best illustrated by some of the molded solid buttons, insulators, phonograph records, brush-backs, magneto distributors, knife-handles, pressed plates, and other manufactured objects you see here before you, many of which have been molded in the hot hydraulic press, without any after-treatment. Some of these articles have been molded and finished in a few minutes' time; others of large size require some longer heating.

Here is a third rail insulator block, molded from a mixture of asbestos fiber and Bakelite. From its excellent appearance, you would never imagine that it has had two years of strenuous service for heavy passenger traffic on the third rail system of the New York Central lines, exposed to rain and sun and all the extreme conditions of our variable climate.

Molded compositions of ordinary asbestos and Bakelite, containing less than one-third of Bakelite, have shown on the Riehlé testing machine tensile strengths as high as 4490 lbs. per square inch, and by selecting carefully the fibrous material still better results can be obtained.

The following electric tests will give a general idea of the dielectric value of Bakelite and some of its composition:

Composition. Different varieties of transparent "C" made specially for electrical purposes by hardening liquid "A" on a glass plate in a stove:	Thickness testing piece in millimeters.		Volts per millimeter, at puncture. Tested with a 50 kilowatt transformer, raising voltage gradually so that puncture occurs within 20 to 30 seconds.
Sample 1	1.78		17,400
Sample 2	2.18		14,200
Sample 3	2.60		13,400
		Punctured at	
Sample 4	0.43	16,750	38,800
Sample 5	0.9	23,300	28,000
Sample 6	0.95	25,600	26,900
Molded composition:			
70 Asbestos	8		
30 Bakelite	8	..	8,500
Molded composition wood flour and Bakelite	7.9		11,000
Impregnated blotting paper, hardened in a hot hydraulic press	3.66	102,000	27,880
Pressed paper impregnated with Bakelite	1.6	53,700	33,500

Some other tests (Electrical Testing Laboratories of N. Y.) have shown an unusually high specific inductive capacity, which makes the material very suitable for electrical condensers.

Pressed paper, impregnated with Bakelite, has been recommended in Germany for the manufacture of electrostatic machines. Its value for this purpose may reside in the fact that it withstands rather well the action of ozone, which is not the case with resins, or with hard rubber. In fact, hard rubber is known to coat itself by and by with an extremely thin film of sulphuric acid, due to slow oxidation of the sulphur. This sulphuric layer, although microscopically thin, causes considerable disturbances for some electrical applications. The impregnation of electric coils with Bakelite is now regularly practised on an industrial scale by several electric manufacturing companies. Its advantages for this purpose are obvious on account of the fact that in case of an increase of temperature, through overload or otherwise, the impregnating material cannot melt; but there is another important factor, namely, this substance, notwithstanding its good electric insulating properties, is a better conductor of heat than the resinous materials or varnishes generally used for the impregnation of dynamos or motors, so that the generated heat is better conveyed to the outside. At any rate, it has been observed that coils impregnated with Bakelite heat up much less than others impregnated with resinous bodies.

Bakelite has rendered excellent service as a glue;

one of its latest applications on a commercial scale is shown by these brushes, of which the bristles are held together with this binding material, which is indifferent to any of the solvents used in paints, varnishes, paint removers and to soap or hot water. It is cheaper and easier to apply than rubber, which has lately been used extensively in the United States for the same purpose. Furthermore, the hardening can be conducted at temperatures so low that white bristles are not discolored.

Let me draw also your attention to these samples of fancy articles, like cigar holders and pipe stems, made of "C," perfectly transparent. Some have the color of amber; others are as colorless as glass. You will notice that they are entirely devoid of odor or taste, even if you rub them. If I insist on this point, it is merely to eliminate an erroneous impression, which has gained some ground, that Bakelite has a particular smell. If there was any smell at all, it would only show that the transformation in C had not yet been complete.

As chemists, you are undoubtedly more interested in the application of Bakelite for laboratory work, or for chemical engineering purposes. Time forbids me to take up the subject in detail. But I may state that a dilute alcoholic solution of "A" finds many uses in the laboratory. Dipping or spraying of metallic objects in or with a solution of the kind, followed by treating in a stove at a temperature of about 120° C. or above, provides them rapidly with a hard protective coating. The time of hardening varies from one minute to half an hour or more, according to the available temperature. If blisters are caused, this indicates that the solution is too thick. This gives us a very economical means for transforming an ordinary sheet-iron-kitchen-gas-oven, which can be purchased at any hardware store for one to two dollars, into a very efficient substitute for the expensive copper drying stove.

Leaks or cracks in glass apparatus can easily be made tight by the skilful application of this solution. In certain cases, asbestos paper or tape, used in conjunction with varnish or Liquid A, will prove an excellent reinforcement.

There is a special variety of Liquid A, which can easily be mixed with asbestos fiber, or clay, or silex powder or baryta, so as to make a very soft dough-like-mass.

If I apply this soft mass to a hot steam pipe, it will stiffen rapidly, until it becomes as hard as stone. By the fact that it contains a base hardening agent, the hardening can take place easily at temperatures as low as 75° C., although higher temperatures will give quicker results. This makes an excellent mixture for spreading on the surface of cast iron pipes or other parts of machinery which have to be protected against the corrosive action of some chemicals. Here is, for instance, a part of an iron casting, the inside of which has thus been protected by applying this paste as a $^1/_4$-inch inside lining. These protected iron castings have been used in a large electrolytic plant, where they have been submitted for more than a year, day and night, continuously to contact with rapidly moving hot brine and hot chlorine, at temperatures of about 70° C. For such purposes it is always better to apply the material abundantly, because it is very difficult to spread a thin film of any material so uniformly that there should not exist some unprotected places where corrosion can occur.

For certain chemical uses like digesters, the possibility of chemical corrosion is augmented by mechanical abrasion, due to the friction of moving liquids or solids. For such purposes, there exists a simple and efficient way for lining the vessel with acid-proof bricks, held together with Bakelite cement. This is accomplished in a somewhat similar way as porcelain-lined ball mills are made, with that difference that the walls of the vessel ought to be first lined with a thin sheet of asbestos paper, impregnated with liquid A; on this the brick lining is inserted and fastened with liquid A or better with a cement made with liquid A and some inert filling materials, like clay, baryta, or powdered silex, or asbestos. This liquid mixture is easily applied, and then a suitable heater, for instance a gas-stove, is introduced in the vessel, so as to raise the temperature of the lining to at least 80° C., or higher, until the polymerization into C has taken place.

Whenever asbestos is used as a filling material, it should not be forgotten that Canadian asbestos is easily attacked by acids. Amphibole asbestos is considerably more resistant to acids; unfortunately, it lacks strength and fibrous qualities. Green Cape asbestos resists acids well and has a good strong fiber, but is more expensive.

THE "KAISER WILHELM INSTITUT FUER PHYSIKALISCHE CHEMIE UND ELEKTROCHEMIE" IN DAHLEM NEAR BERLIN.

By William D. Harkins.

Received October 4, 1911.

On October 1st Professor F. Haber began his work as Director of the new Kaiser-Wilhelm Institute für physikalische Chemie und Elektrochemie at Dahlem near Berlin. The buildings of the Institute, work upon which was begun during the present summer, are being erected by the Prussian government working in conjunction with the "Koppel-Stiftung for the purpose of improving the intellectual relations of Germany with other lands."

The "Koppel-Stiftung" which was founded in Berlin some years ago by Geheimer Kommerzienrat Leopold Koppel, and which until now has maintained the German School of Medicine in Shanghai and the American Institute in Berlin, will provide the funds for the erection of the new Institute and will also give thirty-five thousand marks annually for its maintenance during a period of ten years. The Prussian government has provided the site which is situated at the terminus of the new underground railway from the center of Berlin to Dahlem, and has endowed the Institute with the sum of fifty thousand marks annually.

The Institute will be controlled by a board consisting of two representatives of the German government, two representatives of the Koppel-Stiftung, and the Director of the Institute. The Director has an absolutely free hand in the choice of his work, his fellow workers, and his assistants.

For the admission of investigators who wish to follow their own lines of investigation in the Institute with their own means, the Director must have the assent of the board of control.

The Institute will consist of scientific and technical departments in separate buildings. The building of the scientific department is 600 square meters in ground area, and has a basement entirely underground containing constant temperature rooms. On the ground floor are the professor's laboratory and consulting room, the offices, the calibrating room in which are to be kept the necessary laboratory standards, the mechanic's shop, and a lecture theatre to seat twenty-five persons. Further lecture rooms are not provided in the building as *teaching in the ordinary sense is not contemplated in the Institute.* The first floor will be devoted to the library, chief assistant's room, glass-blowing room, and a laboratory for eight research men. On the second floor are the living rooms for the mechanic and his family, since the mechanic also acts as caretaker. This floor also contains rooms for photochemistry, for scientific collections, and work places for several more research workers.

Professor Haber and Staff at Karlsruhe, 1911.

The building is connected by a corridor with the technical department whose important feature is the machinery hall with a floor space of two hundred square meters. This hall is surrounded by smaller rooms for chemical preparations, high voltage and heavy current work, and a blacksmith shop. The ground floor of the technical building contains a consultation room and the laboratory of the assistant in charge of that department. On the first floor are the living accommodations for two assistants and an engine-man, and also a room for the serving of refreshments.

The Director's house will be erected in the grounds of the Institute.

Although there exists no stipulation on the point, *it may be taken as a rule that, on account of the fact that no teaching as such is to be undertaken, only such students will be admitted by the Director as have already finished their normal university course and desire a wider experience in scientific research.* This will mean that students who come directly from American universities should have the degree of Doctor of Philosophy in Chemistry, or Physics, or an equivalent training. There are no restrictions whatever as to the nationality of the men admitted by the Director.

The Director of the Institute, Professor Haber, was born in Breslau in 1868, and obtained his Ph.D. in Berlin in 1891. After obtaining his degree he spent several years, partly in technical work and partly in securing further scientific training. In 1894 he went to Karlsruhe and was appointed Privat-dozent in Chemical Technology in 1896, and ausserordentlicher Professor in 1898. In 1902 he was sent to America by the Bunsen Society of Applied Physical Chemistry to study the system of chemical instruction and the condition of electrochemical industries in the United States. In 1906 he was appointed to the post of ordentlicher Professor in Physical and Electrochemistry in Karlsruhe, where he built up the best equipped research laboratory of Physical Chemistry in the world. Students from all parts of the world were attracted to this laboratory to such an extent that its accommodations were insufficient to allow all of them to enter, even although Professor Haber admitted as many as forty men at one time as research workers. What was most remarkable was that he personally directed the work of all these men, and often aided them in their experimental work. In 1907 he was called to take the place of Lunge in Zurich as professor of chemical technology, and in 1909 he was asked to undertake the control of one of the largest chemical works in Germany, but he declined both of these appointments.

Professor Haber introduced into Germany the rational method of instruction in elementary chemistry as embodied in the laboratory outline written by Alexander Smith. This book was translated into German by Professor Haber and Fritz Hiller.

The two books, 1898 Lehrbuch der technischen Elektrochemie auf wissenschaftlicher Grundlage (now out of print), 1905 Thermodynamik technischer Gasreaktionen (English edition 1908), together with numerous contributions to the *Zeitschrift fuer Elektrochemie*, Wiedemann's *Annalen*, and the *Zeitschrift fuer physikalische Chemie*, constitute his literary activities.

One of Professor Haber's most important researches was that upon the ammonia gas equilibrium at high temperatures. This work resulted in the development of a commercial method for the manufacture of pure ammonia directly from the elements by the use of osmium or uranium as a catalyzer. Another important series of researches was that upon the properties of flames, including the gas equilibria involved, the ionization and conductivity of the gases, and the action of the ions as catalyzers. He has spent much time during the last few years upon the study of the escape of electrons from the reacting surfaces of metals, and the effects of electrons upon gas equilibria and upon the velocity of chemical reactions. His other recent researches have been mostly upon the following subjects: the electromotive force of the oxyhydrogen cell at high temperatures; the oxidation of nitrogen in the high potential arc; a gas refractometer for the optical analysis of gases; according to Rayleigh's principle, electrical forces at phase boundaries; the corrosion of iron by stray currents from street railways; the reduction of hydroxylamine; the use of solid materials such as glass and porcelain as electrolytes; the equilibrium between magnesium chloride and oxygen; electrode potentials and electrolytic reduction; the laboratory preparation of aluminium; the preparation of hydrogen peroxide by electrolysis; experiments on the decompositions and combustion of the hydrocarbons; and autoxidation.

The writer wishes to thank Dr. Fritz Hiller, of Berlin, for the greater part of the information contained in this article. The statements in regard to the purposes and government of the Institute are official.

UNIVERSITY OF MONTANA,
MISSOULA.

SCIENTIFIC SOCIETIES

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

The Annual Meeting of the Institute will take place in Washington, December 20th to 23d, with headquarters at the New Willard Hotel. After the regular business sessions and reports of committees, the following program will be presented:

PROGRAM.

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NEW WILLARD HOTEL, WEDNESDAY, DECEMBER 20TH, 9.30 A.M.

Address of welcome.

Business session.

Report of committees.

The following papers will be presented:

"Advances in Testing Explosives," Clarence Hall.

"Distribution of Power in Portland Cement Manufacture," Richard K. Meade.

"Manufacture of C. P. Acids," J. T. Baker.

"Manufacture of Gelatin," Ludwig Thiele.

"The Natural Bituminous Rocks of the United States," S. F. Peckham.

EXCURSION, 1.30 P.M.

Visit to Bureau of Standards:

The members of the Institute and their guests will be divided into three parties, making the following inspections:

(1) Inspection of adjustment of pyrometers, thermometers, pressure gauges and similar instruments.

(2) Inspection of the standardizing of weights and measures.

(3) Inspection of liquid air apparatus to be in operation for the benefit of the visitors.

MEETING, 8.00 P.M.

Address of the Retiring President, Dr. F. W. Frerichs.

(*a*) "Manufacture of Chloroform from Alcohol."

(*b*) "Manufacture and Testing of Shipping Cylinders for Liquid Ammonia with the Design of Valve."

"The Manufacture and Testing of Carbonic Acid Cylinders," John C. Minor, Jr.

THURSDAY, DECEMBER 21ST.

EXCURSION.

U. S. Proving Grounds at Indian Head.

(Notice should be given to the Secretary immediately, stating nativity, citizenship and business connection, by those who desire to make this visit, as same must be submitted for approval.)

The Proving Grounds comprise plants for contact sulphuric, nitric and mixed acids, the nitration of cellulose and recovery drying; powder presses, mines and heavy artillery.

DINNER IN NEW WILLARD HOTEL, 7.00.

FRIDAY, DECEMBER 22ND, 9.30 A.M.

Installation of officers.

Business session.

SYMPOSIUM ON THE UNITED STATES PATENT SYSTEM.

"The United States Patent Office," by E. B. Moore, Commissioner of Patents.

"Patent Office Procedure" (Practice of Patent Law up to the issue of the Patent), Edward T. Fenwick, of Mason, Fenwick and Lawrence.

"Protection of Inventions by Patents: Existing Defects and Remedies Therefor," by W. D. Edmunds, of Edmunds and Peck.

"Patent Litigation," by R. N. Kenyon, of Kenyon and Kenyon.

2.30 P.M.

Reception at the White House.

The President will receive the members of the Institute in the East Room of the White House.

3.00 P.M.

Visit to the Patent Office.

8.00 P.M.

"The Adaptation of the Centrifugal Pump to Chemical Service," (illustrated with lantern slides), by F. G. Wheeler.

Business session.

SATURDAY, DECEMBER 23D, 9.30 A.M.

Excursion (alternative):

(*a*) Steel Plant at Sparrows Point, Baltimore.

(*b*) Cement Plant of Tidewater Portland Cement Co.

Association of American Portland Cement Manufacturers. Dec. 11–13. Annual meeting at New York City. Secy., Percy H. Wilson, Land Title Bldg., Philadelphia, Pa.

American Society of Agricultural Engineers. Dec. 27–29. Annual meeting at St. Paul, Minn. Secy., J. B. Davidson, Ames, Iowa.

NOTES AND CORRESPONDENCE.

MANGANESE IN STEEL.

To the Editor of the Journal of Industrial and Engineering Chemistry:

As a suggestion to those using Walter's persulfate method for manganese in steel, the writer has found that by using 10 cc. of a 15 per cent. aqueous solution of ammonia persulfate instead of adding the dry salt to the HNO_3 solution of the steel in the test tube, the tendency to foam and the color to fade is overcome, and a much clearer solution results. Also 5 cc. of a $AgNO_3$ solution containing 4 grams per liter are used instead of the usual 15 cc. containing 1.33 grams per liter. This keeps the volume of the solution below 30 cc.

This method also gives good results by titration with sodium arsenite, the only difficulty being a yellowish brown tinge toward the end of the reaction, making the end point rather hard to distinguish without a great deal of practice. The writer is now at work trying to find a way of obviating this difficulty, making the end reaction sharp and distinct.

GORDON L. VON PLANCK.

PITTSBURG, CALIFORNIA,
November 2, 1911.

ELECTROLYTIC "ALTERATIVE."

To the Editor of the Journal of Industrial and Engineering Chemistry:

Now that so much work has been done to render the copper electrolytic process more efficient by the addition of various substances to the electrolyte it seems regrettable that no more appropriate title than that of "addition agents" has come into use. In this connection the word "alterative" seems to be somewhat more suitable, or to be more explicit, "electrolytic alterative."

J. L. HACKETT.

FLUSHING, N. Y.,
October 27, 1911.

WESTERN PHOSPHATE DEPOSITS.

Until recently it had been generally assumed that the phosphate deposits of South Carolina, Florida, and Tennessee afforded an "inexhaustible" supply, but recent estimates by the Geological Survey show that at the present rate of increase in phosphate mining these eastern deposits are likely to be exhausted within a generation.

The discovery of the western phosphate beds, therefore, constituted a most important find, and though the first reconnaissance of these deposits by the Geological Survey showed their considerable extent, the more detailed study and exploration, with additional discoveries made by the Survey during the last three years, have shown that the field is probably the greatest in the world. Recent geological study of the phosphate-bearing strata indicate the probably still greater extension of the phosphate area. The northernmost portion of the beds first discovered was in Wyoming, but an outcrop of the same character and in the same geologic formation was found last year in Montana, some 160 miles farther north, so that Survey geologists believe that workable phosphate beds may be found in many other places.

The Geological Survey has just published a bulletin embracing three reports on western phosphate fields, one covering a portion of the Idaho phosphate reserve, by R. W. Richards and G. R. Mansfield, another on rock phosphate near Melrose, Mont., by Hoyt S. Gale, and a third being a reconnaissance report on the phosphate deposits in western Montana, by Eliot Blackwelder. The report by Messrs. Richards and Mansfield includes a detailed description of the Idaho field, the investigations having been made by townships, the outcrops examined, and the tonnage of high-grade phosphate rock estimated. Tonnage estimates were made of the phosphate rock in nine townships, and in no township was there found to be less than approximately 60,000,000 tons of high-grade phosphate rock, containing for the most part from 50 to 82 per cent. phosphoric acid.

One of the townships examined contains an estimated 293,000,000 tons of phosphate rock, the net result of the Survey's work showing an approximate tonnage of 2,500,000,000 long tons with 70 per cent. phosphoric acid. Nor does this include the tonnage of the Montana phosphate withdrawals, which aggregate nearly 34,000 acres.

Mr. Gale's report is a brief description of his discovery last year of the Montana deposits near Melrose, withdrawals of which were immediately made by the President. The Survey's tests of a number of samples collected by Mr. Gale show the rock to be high-grade, approximately equivalent to 75 per cent. phosphoric acid. The thickest beds are 6 or 8 feet in thickness. A 6-foot bed would contain approximately 21,000 long tons to the acre.

"One of the most important considerations in connection with the discovery of phosphate rock in western Montana," says Mr. Gale, "is its significance as to the probable extent of the western phosphate fields, for it now appears probable that similar deposits may extend over a large part of western Montana. Their nearness to the large copper smelters is important, for these smelters produce great quantities of sulphuric acid and sulphurous acid fumes which are usually allowed to go to waste through the smokestack of the plant. Reduction of phosphate rock by means of sulphuric acid appears to offer what is perhaps the largest commercial use for these waste products of the smelters." Mr. Gale quotes a report showing the daily loss at the Anaconda smelter alone of about 3,800 tons of sulphuric acid.

Mr. Gale suggests a further innovation in the treatment of phosphate rock which would greatly reduce the transportation charges that at present stand in the way of development. By this process a ton of concentrated phosphate would equal three tons of ordinary superphosphate. The fertilizer distributor would therefore pay freight on one ton where he now pays it on three.

The report calls attention to the fact that under the present mining law there appears to be no adequate provision for the disposal of phosphate lands, and that it is presumed that Congress will, in the near future, pass some well-considered measure to cover this need.

Mr. Blackwelder's contribution on phosphate in western Wyoming is a preliminary report and shows large and widely distributed deposits. He also mentions the presence of very great quantities of low-grade rock, which in course of time will doubtless be mined. For instance, in the Snake River canyon in western Wyoming he noted a total thickness of phosphatic beds exceeding 40 feet, of which about 29 feet contain more than 30 per cent. phosphoric acid and some beds contain 70 per cent. or more.

POTTERY PRODUCTION.

The manufacture of pottery of various kinds has grown to be an enormous industry in the United States, and it was in a highly prosperous condition in 1910, according to a report by Jefferson Middleton, United States Geological Survey. In 1899 the value of the pottery products of the United States was $17,250,250. The product for 1910 was greater by $16,534,420, a gain of 95.85 per cent. During the same period the imports increased 40.73 per cent.

The pottery products of the United States, as classified by Mr. Middleton, consist of red earthenware (flower pots); yellow and Rockingham ware (culinary utensils, teapots, etc.); cream-colored ware, white granite ware, semiporcelain and semivitreous ware, and china in its various forms (general household wares, such as table ware, toilet sets, etc.); sanitary ware (bathtubs, lavatories, washtubs, etc.); and miscellaneous wares, including art pottery made under various trade names, chemical pottery, jardinieres, pins, stilts, and spurs for potters' use, porcelain door knobs, porcelain hardware trimmings, porcelain lighting appliances, smoking pipes, toy marbles, turpentine cups, umbrella stands, filter stones and tubes, and shuttle eyes and thread guides.

The product of most importance is white ware, which includes general household ware, though it is produced in only 8 states. This product was valued at $14,780,980 in 1910, compared with $13,728,316 in 1909. Ohio was the leading producer, reporting a value of $9,730,408 for 1910. West Virginia was second and New Jersey third. White ware composed 43.75 per cent. of all pottery products.

Chinaware, the highest grade of general ware, though comparatively small in value of production ($1,962,126 in 1910), showed a gain of $195,306 in 1910. It was produced in but 3 States in that year. New Jersey was the leading State, reporting ware valued at $1,131,412. New York was second and Pennsylvania third. China constituted 5.81 per cent. of all pottery products in 1910.

Sanitary ware was valued at $6,758,996 in 1910, which was a gain of $769,701 over 1909. It was produced in 9 States. New Jersey was by far the largest producer, the value of its output being $4,955,066. West Virginia was second and Indiana third. Sanitary ware formed 20 per cent. of the value of all pottery products.

Porcelain electrical supplies were produced in 10 States in 1910, of which Ohio was the leader, reporting ware valued at $1,277,144. These wares composed 11.23 per cent. of the total value of pottery products.

Red earthenware was made in 33 States to the value of $854,196, Pennsylvania being the largest producer. Ohio was second and Massachusetts third.

Stoneware and yellow and Rockingham ware were valued at $3,796,688 and were made in 28 States. This is the only branch of pottery production that showed a decrease in 1910. Ohio, as for many years, was the leading State in the manufacture of these wares, reporting 43.84 per cent. of the total. Illinois was second and Pennsylvania third.

Ohio is the leading pottery-producing State in the Union, reporting a value in 1910 of $14,794,712, or 42.31 per cent. of the whole. New Jersey was second, with wares worth $8,588,455, or 25.42 per cent. of the total. West Virginia was third, with wares valued at $2,675,588. The 5 leading States—Ohio, New Jersey West Virginia, Pennsylvania and New York—produced 88.60 per cent. of the total.

Imports of pottery in 1910 were valued at $11,127,405, an increase of $520,193, or 4.90 per cent. The exports of pottery, which are confined almost exclusively to the lower grades of ware, increased $177,994, or 20.61 per cent. over the 1909 exports.

SAND-LIME BRICK.

The sand-lime brick industry was in a prosperous condition during the year 1910, according to statistics compiled by Jefferson Middleton, of the United States Geological Survey. These statistics also show a rapid development of the industry in recent years. The value of the production in 1910 was $1,169,153, against $1,150,580 in 1909 and only $155,040 in 1903.

Michigan led in 1910, as for several years, and reported products valued at $240,649; this was a gain of $22,423, or 10.28 per cent., over 1909. Michigan's output constituted about one-fifth of the total value of all sand-lime products in 1910. Minnesota, the second in rank, producing $154,250 worth, was the state to show the largest increase over 1909—$41,181, or 36.42 per cent. New York was third in output, Florida fourth, and Pennsylvania fifth. Of the states for which totals are compiled by Mr. Middleton Indiana showed the largest proportional gain, 93.70 per cent. Of these States only two showed a decrease in value of the product, Iowa $16,941, or 35.14 per cent.; and New York $1,252, or 1.39 per cent.

EFFICIENCY OF SAND-LIME BRICKS.

The process of making sand-lime brick was invented in Germany, where it probably has had its greatest development. Observations made there seem to prove that sand-lime brick is a building material which will resist shining soot. Three years ago an inn was built in Greifenhagen, in which sand-lime brick was used for everything but the lining of the chimney flues, which were built of common brick because at that time the question whether sand-lime brick was equally resistant to fire had not been settled. In spite of the fact that lignite briquets were burned, shining soot was found in the flues in a short time, and the flue bricks were permeated as high as the rafters of the ground floor. When the flues were pulled down it was found, however, that the sand-lime brick were entirely unharmed and white in color, in spite of the fact that the brick walls were only about 4$^1/_2$ inches thick. If this experience is repeated elsewhere, it is stated, the fact will be established that sand-lime brick is the best building material to withstand shining soot.

IRON AND STEEL INDUSTRY, 1910.

The iron and steel industry in the United States broke all previous records in 1910, according to Ernest F. Burchard, of the United States Geological Survey. The iron ore production was 56,889,734 long tons, the pig iron production 27,303,567 tons, and the steel production 26,094,919 tons. These figures show increases over the production in 1909 of iron ore 5,734,297 tons, pig iron 1,508,096 tons, steel 2,139,898 tons. The following table shows the enormous growth of the iron and steel industry in the United States since 1900:

	Iron ore.	Pig iron.	Steel.
1900	27,553,161	13,789,242	10,188,329
1905	42,526,133	22,992,380	20,023,947
1906	47,749,728	25,307,191	23,398,136
1907	51,720,619	25,781,361	23,362,594
1908	35,924,771	15,936,018	14,023,247
1909	51,155,437	25,795,471	23,955,021
1910	56,889,734	27,303,567	26,094,919

The value of the iron ore produced in 1910 was $140,735,607, as against $109,964,903 for 1909, and that of pig iron was $425,115,235, as against $419,175,000 in 1909.

Iron ore was mined in 28 States in 1910. The following table shows the production of the five leading States:

	Long tons.	Value.
Minnesota	31,966,769	$78,462,560
Michigan	13,303,906	41,393,585
Alabama	4,801,275	6,083,722
New York	1,287,209	3,848,683
Wisconsin	1,149,551	3,610,349

The five leading States in pig iron production were as follows:

	Long tons.	Value.
Pennsylvania	11,272,323	$180,695,338
Ohio	5,752,112	88,122,356
Illinois	2,675,646	42,917,362
Alabama	1,939,147	23,754,551
New York	1,938,407	32,410,165

During 1910, of the 451 iron ore mines in operation, 191 mines produced over 50,000 long tons each, the largest quantity produced by a single mine being 3,190,093 tons, by the Hull-Rust mine, of the Mesabi range, Minnesota. Nine mines in Minnesota, besides one group of mines in Michigan and one group in Alabama, produced more than 1,000,000 tons each, the second greatest production being 1,769,067 long tons by the Red Mountain group of mines, near Birmingham, Alabama. Twenty-five mines produced more than 500,000 tons each.

Importations of iron ore in 1910 were the greatest in the history of the industry, being 2,591,031 tons, valued at $7,832,225. Exports were 644,875 tons valued at $2,074,164. Figures showing the foreign production of iron ore are not yet available for 1910, but the following table for 1909 shows the supremacy of the United States in iron mining.

United States	long tons	51,155,437
Germany and Luxemburg	metric tons	25,506,000
United Kingdom	long tons	14,979,979
France	metric tons	11,890,000
Cuba	long tons	1,417,914

No other country produced so much as a million tons. It will be seen that the United States produced nearly one-half of the total of the world's output.

In steel production in 1910, Pennsylvania led all States, with 13,207,539 long tons and Ohio came second with 5,050,608 tons. The total production of the United States was 26,094,919 tons.

BAUXITE AND ALUMINUM PRODUCTION.

The United States Geological Survey reports that the 1910 output of bauxite in the United States was 148,932 long tons, valued at $716,258. The average price at the mines has been: 1908, $5.06; 1909, $5.26; 1910, $4.81. Bauxite is principally used in the production of metallic aluminum, and in the manufacture of the artificial abrasive, alundum, at Niagara Falls. This abrasive is made in the electric furnace by fusing calcined bauxite. Experiments are also being made in admixing bauxite with other materials for making refractory brick, which for linings far exceeds the life of silica or fire-clay bricks.

The world's production of bauxite in 1909 total 270,581 tons, valued at $949,924, of which the American share was 129,101 tons, worth $679,447. The French output was 128,099 tons, worth $251,188.

The growth and magnitude of the aluminum industry in the United States are shown in the fact that only 83 pounds were produced in 1883, 3,000 pounds in 1886, 4,000,000 pounds in 1897, 17,211,000 pounds in 1907, 34,210,000 pounds in 1909 and 47,734,000 pounds in 1910. The American exports of aluminum and its manufactures increased from $364,521 in 1906 to $949,215 in 1910.

Under the Payne-Aldrich tariff act of August, 1909, aluminum scrap, and alloys of any kind in which aluminum is the component material of chief value, in crude form, are dutiable at 7 cents per pound, and plates, sheets, bars, and rods at 11 cents per pound instead of 8 cents and 13 cents, respectively.

The president of the Aluminum Company of America states that business in 1910 fell off on account of curtailed production in steel-making, in which it is used for deoxidizing and in the curtailed automobile business. "Large stocks accumulated and are still accumulating. Some plants have been cut back half and unless the demand improves still further cutting back will be necessary. The aluminum cooking utensil business was good. Although a new (aluminum) sheet-rolling mill was built in Niagara Falls in 1910, it was not put into operation, on account of the falling off in business, but as it was built to meet future requirements, it is expected that the time will come when the mill will be required."

The following is a summary of an article which appeared in the *Frankfurter Zeitung* of August 10:

"The development of the aluminum industry has been unusually rapid, the world's production having risen from 11,500 metric tons in 1905 to 24,200 metric tons in 1909, and 34,000 metric tons in 1910. The distinctive feature about the aluminum trade is that it is in the hands of only 12 companies, of which 5, *viz.*, the Aluminum Industrie Akt. Ges., of Neuhausen, the Société Electro-Métallurgique Française, of Froges, the Compagnie des Produits Chimiques d'Alais et de la Camargue, of Salindres, the British Aluminum Company (Ltd.), and the Aluminum Company of America, account for nine-tenths of the total output."

WORLD'S CONSUMPTION OF BEER, WINE AND SPIRITS.

More beer is consumed in the United States than in any other country of the world, and more distilled spirits than in any other country except Russia. The quantity per capita consumed in the United States is not, however, in the case of beer, as great as in Belgium, United Kingdom, Germany, or Denmark, while our per capita consumption of distilled spirits is less than that of Denmark, Hungary, Austria, France, Netherlands, or Sweden. Of wines, the quantity consumed in the United States is below that of Portugal, Spain, Germany, Italy, or France; and the per capita consumption is less than that of France, Italy, Portugal, Spain, Switzerland, Austria, or Hungary.

The following table, compiled from official sources by the Bureau of Statistics, Department of Commerce and Labor, shows in millions of gallons the consumption of malt liquors, wines, and distilled spirits, respectively, in the principal countries of the world for which statistics of this character are published and the per capita consumption in each instance, the figures being for the latest year for which statistics are available.

	Consumption.					
	Malt liquors.		Wines.		Distilled spirits.	
Countries.	Million gallons.	*Gallons per capita.	Million gallons.	Gallons per capita.	Million gallons.	Gallons per capita.
United States (1910)	1,851.3	20.09	60.5	0.66	133.5	1.45
United Kingdom (1909)	1,397.3	31.44	15.2	0.31	40.1	0.96
Germany (1909–10)	1,703.5	26.47	74.6	1.16	94.2	1.48
France (1909)	375.0	9.51	1,541.4	39.36	70.9	1.81
Austria (1908–9)	492.9	17.17	178.6	6.34	54.7	1.81
Belgium (1909)	411.7	55.2	9.1	1.21	10.7	1.42
Russia (1908)	231.4	1.46	no data	no data	232.7	1.45
Spain (1909)	no data	no data	345.9	18.23	no data	no data
Sweden (1908–9)	72.3	13.31	no data	no data	8.6	1.57
Switzerland (1909)	64.6	18.00	52.2	14.55	3.6	0.99
Denmark (1909)	61.7	22.98	no data	no data	8.0	2.97
Italy (1909)	17.4	0.51	1,012.0	31.17	26.1	0.76
Bulgaria (1909)	3.2	0.75	34.9	8.19	0.6	0.13
Hungary (1908–9)	55.7	2.90	98.6	4.76	43.7	2.11
Netherlands (1909)	no data	no data	2.3	0.40	10.8	1.84
Norway (1909)	11.8	5.02	no data	no data	2.0	0.87
Portugal (1909)	no data	no data	146.3	27.39	no data	no data
Roumania (1909)	4.9	0.72	33.7	5.02	6.7	0.96
Servia (1909)	2.9	1.02	10.5	3.70	no data	no data
Australia (1909)	56.9	13.20	5.6	1.30	4.6	1.07
Canada (1909–10)	47.4	6.36	0.9	0.12	7.3	0.97
Cape of Good Hope (1909–10)	3.3	1.32	3.5	1.44	1.2	0.53
Transvaal (1909)	3.9	2.88	0.5	0.38	0.8	0.67

REPORTS ON STREAM FLOW.

The United States Geological Survey has announced the publication of four reports on the flow of streams in the United States. They are designated as Water-Supply Papers 265, 266, 267 and 268. The first-mentioned relates to rivers in Minnesota, Wisconsin, North Dakota, Illinois, and Iowa, which drain either into the Mississippi River or northward into Canada. The second relates to rivers draining into the Missouri, the streams being located in Montana, Wyoming, North Dakota, Colorado, Nebraska, and Missouri. The third comprises those streams draining into the lower Mississippi mainly through Arkansas and Red Rivers, the streams being located in Colorado, New Mexico, Arkansas, Missouri and Mississippi. The fourth gives information concerning streams draining into the western part of the Gulf of Mexico, such as the Rio Grande and the Pecos.

The records contained in these reports show the flow of the rivers for each day during the year 1909 as measured by employees of the Geological Survey at permanent stations maintained along the streams. They are essentially a record of the performance of those streams and they furnish an account of the water resources available for use in the regions in which the records were made.

Many of those who are unfamiliar with engineering practice do not realize the necessity of procuring information of this kind. The importance of knowing how much water is available for its various uses grows enormously as the United States becomes more thickly settled and as industrial pursuits advance. We need water for domestic supplies and for navigation. The arid West is dependent on it for the irrigation of dry lands. One of the most important features of our industrial prosperity has been the development of water power.

The four reports above described give a faithful record of each river's performance so that the persons or the community undertaking any development of water will know all the facts concerning the supply available.

INDUSTRIAL GAS APPLIANCE LABORATORY.

The Consolidated Gas Company, of New York City, has for several months been concerned in the work of fitting up an Industrial Gas Appliance Laboratory, in the Schleicher Building, corner of Second avenue and Twenty-second street.

The equipment of the laboratory contains, among other things, a six h. p. Otto gas engine, a three h. p. steam boiler, a combination tool-room furnace, clay annealer, melter, round annealer, bar annealer, forge, tool-room forge, oil tempering furnace, oven furnace, tempering furnace, rivet heater, muffle furnace with D. C. motor and fan blower, lead hardening furnace with extra pot for cyanide, muffle furnace with cupelling attachment, portable melting pot, 1,000 pound soft metal furnace with hood, wire basket and thermometer; brazing tables, automobile and wagon tire heaters, 40-gallon butchers' cauldron, 50-gallon cauldron with bottom draw-off, agitator and pump, china kiln, incinerator, oven with damper and thermometer, core-drying oven, japanning oven, aluminum water still, heating machines, positive blowers, confectioners' stoves—one with D. C. motor and blower—making in all 43 appliances standing on the floor. There are 75 bench appliances on metal tables, which, with a few suitably attached to the walls, make a total of 135 devices, all connected, ready for instant demonstration. The appliances on the tables embrace soldering furnaces and self-heating soldering irons, melting furnaces, glue heater, bench forges, rivet heaters, soft metal furnaces, and a great variety of burners, the largest being connected with D. C. motors and fan blowers, consuming about 700 cubic feet of gas per hour. A complete assortment of blowpipes and brazing burners is also in evidence. The appliances are located in sections, each section being served by a 30-light meter, with special reducing device which consists of a straight line control, the figures changing for each 10 feet, and so arranged that the counter can be turned back after each demonstration. Portable baths are also provided, one each for fresh or salt water; and for a cotton seed oil "dip," if one is so inclined. Then there is a portable sawdust drier, and the several things last enumerated are set on casters, so that one can readily be taken to any other appliance, the contiguity of which is needed for a complete demonstration.

PHOSPHATE MINING, 1910.

The mining of phosphate rock for fertilizer showed increased activity in 1910, with the greatest production in the history of the industry. The output was 2,654,988 long tons, against 2,330,152 tons in 1909, an increase of 324,836 tons. Prices, however, were lower, the value of the 1910 output being $10,917,000, or $4.11 per ton, against $10,772,120, or $4.62 per ton, for 1909. Thus while the tonnage in 1910 increased 13.9 per cent., the value of the year's output increased less than 2 per cent. Nearly half of the phosphate rock produced in 1910 was exported, the shipments being 1,083,037 long tons. In 1909 the exports were 1,020,556 long tons. These and other statistics of production, exports, imports, etc., are given by F. B. Van Horn, of the United States Geological Survey, in an advance chapter from "Mineral Resources" for 1910.

According to Mr. Van Horn, there are at present five producing phosphate fields in the United States. In the order of quantity of production they are (1) Florida, (2) Tennessee, (3) South Carolina, (4) Arkansas, (5) Idaho, Wyoming, and Utah.

By far the largest of these fields is the Idaho-Wyoming-Utah field, where enormous deposits of high-grade phosphate rock, recently discovered, are available for mining. The field next in available unmined rock is probably Tennessee, where large areas are underlain by deposits of high-grade rock. Florida has a large reserve tonnage, but at the present rapid rate of mining it will not be many years before the rock will be exhausted.

Marketed Production of Phosphate Rock in the United States, 1901–1910, in Long Tons.

Year.	Quantity.	Value.
1901	1,483,723	$5,316,403
1902	1,490,314	4,693,444
1903	1,581,576	5,319,294
1904	1,874,428	6,580,875
1905	1,947,190	6,763,403
1906	2,080,957	8,579,437
1907	2,265,343	10,653,558
1908	2,386,138	11,399,124
1909	2,330,152	10,772,120
1910	2,654,988	10,917,000

GYPSUM PRODUCTION.

The importance of the gypsum industry in the United States is shown by figures compiled by E. F. Burchard, of the United States Geological Survey. For 1910 the value of gypsum products was $6,574,478 and the amount of gypsum mined 2,375,394 short tons. This was an increase over the figures for 1909 of more than 5 per cent. in tonnage and more than 10 per cent. in value. The value of the imports in 1910 amounted to only $502,111, or less than 8 per cent. of the domestic output.

New York was the largest producer of gypsum, with an output valued at $1,153,977, an increase of $121,327 over 1909. Iowa came second with a value of $943,849, and Michigan third with $668,201.

The bulk of the gypsum produced was manufactured by grinding and partial or complete calcination into plaster of Paris, molding and casting plaster, stucco, cement plaster, fibered plaster, plaster boards, flooring plaster and hard-finish plaster. The best known hard-finish, anhydrous plaster is Keene's cement, which sets very white and hard. It is used as a backing and surface for artificial marble and for ornamental moldings and castings, and its use as a wall plaster is increasing.

Refined grades of plaster are used in dental work, also as cement for plate glass during grinding, for making pottery molds, stereotype molds, and molds for rubber stamps, and as an ingredient in patent cements. A large quantity of gypsum is used in the raw state as a retarder in Portland cement. Considerable quantities are ground without burning and used as land plaster or in fertilizers. Smaller quantities are used unburned in the manufacture of crayons, paper, imitation meerschaum and ivory, calcimines, water paints and tints, and dry colors, notably Venetian reds. When used in excess in mixed paints, gypsum is regarded as an adulterant. The unburned and dead-burned forms of gypsum may be used to a certain extent with oil paints, because they are not very active chemically.

COAL PRODUCTION OF 1910.

For the first time in the history of the United States, the coal mines of the country in 1910 were credited with an output exceeding half a billion short tons, the combined production of anthracite, bituminous coal, and lignite having amounted to 501,576,895 short tons, with a spot value of $629,529,745. This great output according to Edward W. Parker, Coal Statistician of the United States Geological Survey, was attained in spite of the fact that most of the mines in Illinois, Missouri, Kansas, Arkansas, and Oklahoma were closed for nearly six months by one of the most bitterly contested strikes in the history of the industry. The heaviest tonnage mined in any year previous to 1910 was in 1907, when a total of 480,363,424 short tons was produced.

The output in 1910 showed an increase of 40,762,279 short tons, or 8.85 per cent. Prices generally were a little higher in 1910 than in 1909, the average for Pennsylvania anthracite being $2.13 per long ton, against $2.06 in 1909, and the average for bituminous coal was $1.12 per short ton in 1910, against $1.07 in 1909. The total value increased 13.50 per cent.

The output of anthracite in Pennsylvania increased from 81,070,359 short tons, valued at $149,181,587, to 84,485,236 short tons, valued at $160,275,302, a gain of 4.21 per cent. in quantity and 7.44 per cent. in value. The bituminous production, including semianthracite, semibituminous, cannel, splint, and subbituminous coals, lignite, and a small quantity of anthracite from Colorado and New Mexico, increased from 379,744,257 short tons, valued at $405,486,777, to 417,091,659 short tons, valued at $469,254,443, a gain of 9.83 per cent. in quantity and of 15.73 per cent. in value.

The total increase of 40,762,279 short tons in 1910 over 1909 was equal to 20 per cent. more than the entire output of the United States in 1870 and more than half of the total output in 1880.

INCREASING USE OF ELECTRIC FURNACES.

Prof. McWilliams, of the Sheffield University, in a report prepared for the meeting of the British Association at Portsmouth, gives some interesting figures relating to electric steel production. Up to June, 1910, there were about 118 electric furnaces of all types, of which 70 were in use, 10 were not working, and 38 were being built.

There were 77 arc furnaces recorded, of which 29 were credited to Héroult, 17 to Girod, 13 to Stassano, 6 to Keller, and 12 others. Of the induction furnaces there were 14 of the Kjelling type and 15 of the Rochling-Rodenhauser type. The total capacity of all electric furnaces was 350 tons per charge. In June, 1910, there were 29 Héroult furnaces with a capacity of 80 tons in use and furnaces of 50 tons in course of erection, while in June, 1911, there were 43 furnaces with a total capacity of 242 tons.

The output of electric steel in Germany, the United States, and Austria-Hungary in 1910 amounted to almost 112,000 tons, which is an increase of 63,000 tons over the figures of 1909. Those are the only countries for which the exact output of electric steel is published; probably the figures for Sweden, France, Belgium and Italy would also show large gains. The increase will likely be more than maintained in 1911, as more than 30 new furnaces of various types will be started during the year and many that started toward the end of 1910 will put in a full year's work in 1911. England will also, for the first time, appear as a regular producer, with an output of about 13,000 tons.

PRODUCTION OF PRECIOUS STONES, 1910.

It may perhaps be surprising to many people to learn that the United States produces almost every variety of precious stone—from diamonds down. The precious stones produced in this country last year had a value of $295,797, against $534,380 in 1909, according to an advance chapter from "Mineral Resources of the United States," on the production of gems and precious stones in 1910. The large decrease in the output of a few of the more important gem minerals—tourmaline, turquoise, chrysoprase, etc.,—readily accounted for the fall in the value of production. As an instance of this decrease in production, about 8 ¹/₂ tons of rough turquoise were produced in 1910, as compared with more than 17 tons in 1909.

All the diamonds produced in this country in 1910 came from Arkansas and California, the output of Arkansas amounting to about 200 stones. Several diamonds were found in California last year, one of which weighs about half a carat and another between 1³/₄ and 2 carats. The latter is a brilliant, clear, flawless stone, with a tinge of yellow.

Colorado yields some very pretty agates and some are being successfully handled in the tourist trade but a number of these stones sold each year at the summer resorts of the State are imported from Germany, where they have been polished. Others are native stones polished abroad, although some are polished in the United States.

In Montana a sapphire weighing over 4¹/₂ carats has been found. This stone when discovered had very much the shape of a rough diamond crystal, on account of which it had very great refractive power.

MINERAL WATER PRODUCTION.

In 1910 the sales of mineral water in the United States amounted to $6,357,590, the product being 62,030,125 gallons, as reported by George C. Matson, of the United States Geological Survey. Minnesota was the greatest producer, with 9,962,370 gallons, derived from 19 springs. New York was a close second, selling 8,780,903 gallons from 46 springs. Wisconsin, however, obtained the greatest income from her mineral waters, her sales amounting to $974,366; New York was second, with $858,635; and Indiana third, with $514,958. Minnesota's sales amounted to $281,009. Louisiana has only four commercial springs: they produced 2,313,000 gallons.

Maine's output of mineral waters, from 29 springs, decreased 277,370 gallons, but on account of high prices increased in value over 1909, the figures for 1910 being 1,238,171 gallons and $404,539. Of Wisconsin's mineral waters, 2,151,782 gallons were used in the manufacture of "soft drinks." Pennsylvania has 44 springs and produced 2,536,337 gallons, valued at $221,685.

The mineral water trade continues to be prosperous although there was a decrease in output of about 4 per cent. as compared with 1909. The importation of mineral waters in 1910 was 3,306,303 gallons, valued at $983,136.

FLUORSPAR.

Fluorspar, one of the lesser minerals, has come to occupy a comparatively important place in every-day affairs. It is used in the manufacture of glass, of enameled and sanitary ware, in refining antimony and lead, in the production of aluminum, and as a flux in blast furnaces and in the manufacture of steel in basic and open-hearth furnaces. The production of open-hearth steel alone in 1910 was over 15,000,000 long tons. The production of fluorspar, according to Ernest F. Burchard, of the United States Geological Survey, in a report on fluorspar and cryolite just issued, increased from 18,450 short tons in 1900, valued at $94,500, to 69,427 tons in 1910, valued at $430,196. There was an increase in 1910 of 37 per cent. in quantity and 47 per cent. in value over the figures for 1909. The deposits which have been exploited are in Arizona, New Mexico, Colorado, Illinois, Kentucky, Tennessee, and New Hampshire. Illinois is much the heaviest producer. There was also imported in 1910, according to Mr. Burchard, 42,488 short tons, valued at $135,152. Mr. Burchard's report contains, in addition to the statistics of the industry, a discussion of the methods of mining and milling fluorspar, as well as a description of recently discovered high-grade deposits in New Mexico.

THE DEVELOPMENT OF THE EXPORT OF AIR SALTPETER FROM NORWAY.

The export of this article shows yearly a large increase, although the total quantities are not yet very large. According to the review given out by the "Bureau Central de Statistique de Kristiania" the figures in 1000 tons of Norgesaltpeter in the years 1908–1910 are as follows:

Country to which exported.	1908.	1909.	1910.
Sweden	20.5	32	1.4
Denmark	538	256	392.2
Germany	3841	4803	4791
Holland	1270	1149	1687
Belgium	32	136	363
Great Britain	619	2530	4900
France	671	152	683
Spain	55.6	..	168
Italy	..	15	46
Ireland	..	250	200
Russia	..	21.5	100
Africa	5	12	...
U. S. of America	0.5	..	149
West Indies	..	2.2	10
Australia	..	7	39.6
Other countries	..	..	0.1
Total	7052.6	9365.7	13530.3

The total export in 1910, therefore, amounted to 13,530 tons of saltpeter, of which Great Britain was the principal buyer, followed by Germany. All other countries use about one-half the amount exported to Great Britain and Germany. The price of Chile saltpeter has not yet been influenced by the importation of the air saltpeter.

CONCRETE AND CEMENT AT PANAMA.

The Isthmian Canal Commission have issued a statement showing that the total amount of concrete laid for the Panama Canal during the fiscal year 1910–11 was 1,742,928 cubic yards. The cost per cubic yard for concrete in the Gatun Locks was $6.5919; in the Gatun Spillway, $6.7044; in the Pedro Miguel Locks, $4.7040; and in the Miraflores Locks, $4.6826. At Gatun, 73,609 cubic yards of large rock were used, resulting in a saving of $263,137.45, or of 0.2888 cent per cubic yard on each yard of material placed. In the production of stone for the concrete, the cost in bins at Gatun was $2.3403 per cubic yard, and in the storage pile for the locks on the Pacific side, $0.8443 per cubic yard.

Cement for the large part is delivered in barrels to the Atlantic division at a cost of $1.19 at tidewater in the United States, while in the Pacific division it is delivered in bags at a cost of $1.60 at tidewater in the United States per barrel, less credit for return of bags. As approximately 90 per cent. of the bags were returned and accepted, the cement in bags cost $1.01 per barrel at tidewater in the United States.

INVESTIGATION OF POTASH DEPOSITS.

An investigation into possible sources of potash salts in the United States is being made this year by the United States Geological Survey, and as a part of this work the Survey will soon fit up a temporary laboratory at Fallon, Nevada, for the purpose of testing samples of salines from the Great Basin or desert areas.

Samples of such alkaline salts will be tested at this laboratory free of charge if a definite statement of the locality from which they were obtained be sent with the samples. The location should be given by section, township, and range, if possible, otherwise by distance and direction from the nearest post-office or settlement. Samples should be addressed to Hoyt S. Gale, United States Geological Survey, Fallon, Nev. Upon receipt of a request small sample sacks for sending the material by mail will be forwarded from the above address.

If so requested at the time that a sample is submitted for test, the accompanying information concerning the locality of the deposit will be treated as confidential; and the evidence thus obtained is not to be used for the purpose of making land withdrawals.

CORROSION OF SUPERHEATED STEAM PIPING BY SODA.

Mr. F. Westhoff recently reported (*Stahl und Eisen*, June 29, 1911) to the Dusseldorf convention of the Deutsche Giessereitachleute that in a boiler plant working partly with saturated and partly with superheated steam (at 160 lbs. gage), the wrought-iron pipes and cast-iron valves of the superheated steam line were badly attacked after four years' service, whereas the saturated steam line was in excellent condition. Appearances suggested local solvent action. On close examination a whitish matter was found at the corroded places, which, on chemical analysis, proved to be in part at least sodium carbonate. Soda was used for softening the feed, and it seemed that the amount used was rather excessive; $1^1/_2$ days after blowing down the boilers the boiler water showed 21.2 grams soda per 100 liters, or 12.4 grains per gallon. The investigator concluded that soda particles were carried along with the steam, and that in the superheated steam line they could deposit, while with saturated steam the condensation flow prevented deposits. He concludes that this deposited soda corroded the iron.

A STANDARD PORTLAND CEMENT SPECIFICATION.

United States Government work is being looked into by a special committee of government engineers, which has been meeting during the past summer. This committee was appointed to draw up a tentative specification by a conference of government engineers that first met in Washington, D. C., on June 17, 1911. The draft of this specification was submitted later to the conference and proved acceptable in most particulars. The committee was then instructed to consult with the American Society of Civil Engineers the American Society for Testing Materials and other similar bodies as to the practicability of developing a uniform specification that might become a generally accepted standard throughout the United States.

The committee is composed of A. P. Davis, Chief Engineer, U. S. Reclamation Service; J. C. Plant, Supervising Architect's office; Captain W. R. Rose, Corps of Engineers, U. S. A.; Lieut. C. A. Carlson, Corps of Civil Engineers, U. S. N.; S. S. Voorhees, Bureau of Standards; A. E. Phillips, Superintendent of Sewers, District of Columbia; and R. J. Wig, Bureau of Standards.

MINERAL PRODUCTION SECOND ONLY TO AGRICULTURE.

Nearly a third of a billion dollars was added to the wealth of the United States from the mineral production of the western States during 1910, according to the figures of the United States Geological Survey. This includes about $66,000,000 worth of coal, the remaining production, principally metals, having a value of practically a quarter of a billion dollars. The total figures of western mineral production as compiled by the Survey are $313,944,881. This is about one-fourth the total agricultural production of the same area, the proportion between mineral and agricultural production being about the same as for the entire United States. The agricultural production of the western States, derived from figures of the Department of Agriculture, was approximately $1,394,791,000. The area considered includes the belt from the Dakotas south to Texas and the territory westward.

PRODUCTION OF LIME IN 1910.

The total production of lime in 1910, according to figures compiled by Ernest F. Burchard and just given out by the United States Geological Survey, was 3,469,416 short tons, valued at $13,809,290, a slight decrease in both tonnage and value as compared with the figures for 1909. The average price per ton in 1910 was $3.98.

The five leading States in the 1910 production are as follows:

	Short tons.	Value.
Pennsylvania	877,714	$2,440,350
Ohio	415,285	1,647,335
Wisconsin	248,238	959,405
Maine	179,656	893,599
Missouri	193,964	837,681

OIL USED IN PLACE OF COAL.

The small production of coal in California is offset by the enormous increase in the production of petroleum, most of which is used for fuel. The oil produced in California in 1910 aggregated between 65,000,000 and 70,000,000 barrels, which, on the basis of $3^{1}/_{2}$ barrels of oil for each ton of high-grade coal, would be equal to a production of nearly 20,000,000 tons of coal.

The use of petroleum by the transportation and manufacturing industries of California has practically eliminated coal as a steam-raising fuel in the State. Oil is also used in the manufacture of gas which is employed for cooking and for heating residences as well as for lighting. Oil is now also coming into use as a direct fuel for household purposes.

NEW JERSEY'S ZINC PRODUCTION.

The zinc mines, at Franklin Furnace, New Jersey, produced in 1910, according to H. D. McCaskey, of the United States Geological Survey, 308,353 tons of ore for the concentrating mills (producing 263,606 tons of concentrates), and 67,324 tons of crude ore for the smelters. Figured as metallic zinc, the total recoverable output was 137,355,219 pounds of spelter, valued at $7,417,182. The mines are opened by a vertical shaft 965 feet deep, a slope to the 600-foot level, and a shaft 1,500 feet deep on an incline of 47 1/2 degrees. The crushing plant has a capacity of 2,240 net tons per 24 hours and the separator a capacity of 1,344 net tons.

WORLD'S SULPHUR PRODUCTION.

The sulphur industry in the United States in 1910 was confined to the four states of Louisiana, Nevada, Utah and Wyoming, the production of the other states being practically negligible as compared with that of Louisiana. The production of sulphur for 1910, according to W. C. Phalen, of the U. S. Geological Survey, was 255,534 long tons, as compared with 239,312 long tons in 1909. In 1910 there were imported into the United States 30,833 long tons of sulphur, while the exports amounted to 30,742 long tons.

SICILY SULPHUR PRODUCTION.

The total production of sulphur in Sicily during the first six months of 1911 was 182,678 tons, against 185,825 tons during the corresponding period in 1910.

On June 30, 1911, the total stocks of sulphur in Sicily were 527,965 tons, against 586,878 tons at the same date in 1910. The exports of sulphur during the first half-year of 1911 amounted to 287,410 tons, against 240,919 during the first six months of 1910, an increase of 46,491 tons.

SALT PRODUCTION, 1910.

The United States produced 30,305,656 barrels of salt in 1910, valued at $7,900,344, according to the U. S. Geological Survey. This was an increase of 198,010 barrels over the production of 1909 but a decrease in value amounting to $443,487. The six leading producers of salt in 1910 were New York, Michigan, Ohio, Kansas, Louisiana, and California. Nearly 99 per cent. of the salt consumed in the country was obtained from domestic sources, the United States having long been independent of foreign production.

PLATINUM PRODUCTION, 1910.

The entire production of crude platinum from placer mines in the United States for last year, as well as for 1909, came from the States of California and Oregon. This production in 1910, according to Waldemar Lindgren, of the United States Geological Survey, was 390 troy ounces, valued at $9,507, a decrease of 282 ounces and $3,296 compared with the figures for 1909.

INTERNATIONAL MACHINERY AND ENGINEERING EXHIBITION.

An International Machinery and Engineering Exhibition will be held at Olympia, London, from October 4 to 26, 1912, inclusive. This Exhibition is organized by the Machine, Tool and Engineering Association (Ltd.), and the Exhibition offices are at 104 High Holborn, London, W. C.

The projectors of the Exhibition state that it is their purpose to secure, if possible, so comprehensive a display that it will be really representative of the engineering trades throughout the world.

MODIFICATION OF THE DETERMINATION OF NICKEL BY THE ETHER METHOD.

Owing to the length of time necessary for the determination of nickel in iron and steel by the usual ether method which involves solution in nitric acid and several evaporations to dryness and baking prior to the ether separation, I have been working toward a shorter method. This has been found by using hydrogen peroxide as an oxidizing agent in place of nitric acid. By this change in method, determinations can be made in one-fourth the time and with just as consistent accuracy.

Method.—Dissolve one gram of the sample in a mixture of 20 cc. of hydrochloric acid and 5 cc. of water using a 200 cc. beaker. Cover with a watch glass and heat until solution is effected. When the sample is dissolved cool the solution a little, add 20 cc. hydrogen peroxide (washing the sides of the beaker and watch glass) and boil to a small bulk, about 10 to 15 cc. Cool and make ether separation in the usual way.

The nickel is determined volumetrically in the usual way making the solution ammoniacal and titrating with potassium cyanide using silver nitrate and potassium iodide as an indicator.

Carpenter Steel Company,
Reading, Pa.,
October 12, 1911.

John P. Thompson.

GENERAL NOTES.

Dr. Cushman announces the organization and equipment of a Division of Roads and Pavements under the supervision of Mr. Prévost Hubbard, for the past seven years with the U. S. Department of Agriculture, as chief chemist of the Office of Public Roads.

The Division of Roads and Pavements has been assigned adequate quarters in the Institute's new building, which has just been completed, and will consist of two well equipped laboratories—one for physical work in connection with cements, mortars, concrete block, brick, etc., and the other for chemical analysis and investigations of all types of bituminous and other road and paving materials. The equipment consists of the latest approved apparatus, and special apparatus will be added as occasion demands.

Besides the routine examination, inspection, and specification of road and paving materials which will be undertaken by this Division, the Institute particularly solicits correspondence relative to problems connected with the road material industries, in regard to improvements of materials and processes, and the utilization of waste and by-products.

Ground was broken last week for the Wolcott Gibbs Memorial Laboratory of Harvard University. This building, designed for research in physical and inorganic chemistry, will cost when completed about $72,000. It was given and endowed by Dr. Morris Loeb, Mr. James Loeb and many other friends of Dr. Gibbs and the University.

Mr. Arthur H. Blanchard, M. Am. Soc. C. E., consulting highway engineer, formerly of Providence, R. I., announces the removal of his office and laboratory to Broadway and 117th Street, New York City.

Sugar beets in Canada from the 12,000 acres this season are expected to yield 9,000 long tons of sugar, against 7,771 tons from 10,500 acres last year. Canada imported 574,108,164 pounds of sugar, valued at $15,110,740, in the fiscal year ended March 31, 1911.

American imports and exports both made large gains in September, being $125,160,444 and $193,623,232, in value, respectively, advances of $7,895,931 and $27,677,012 over September, 1910.

CONSULAR AND TRADE NOTES.

INTERNATIONAL RUBBER EXHIBITION.

By Consul General John L. Griffiths.

The most interesting feature of the International Rubber Exhibition held in London, June 24 to July 14, was the evidence of the great growth of the rubber industry in the past few years, and the multiplied uses for which rubber is now employed.

The greatest demand for rubber is, of course, in the boot and shoe industry, and in the manufacture of motor and cycle tires. The variety of purposes for which rubber in some form is employed was shown at the exhibition in displays of golf and tennis balls, mackintoshes, fountain pens, air pillows, water beds, cables, buckets, mats, and tiling, etc.

The principal subjects discussed at the conference were rubber cultivation, the preparation of rubber, and rubber manufactures.

The planter, manufacturer, machinist, and chemist were brought into touch with each other and an opportunity afforded for the interchange of views.

The principal countries exhibiting were Brazil, Ceylon, Federated Malay States, Belgium, Holland, Germany, South India, Uganda and the West Indies.

The special medal for the best exhibition of rubber was awarded to the State of Amazonas, Brazil. This exhibition consisted of 20 tons of rubber and 5 tons of caucho ball, representing approximately the one-thousandth part of the rubber passing annually from Manaos. In 1901–2, 19,989 tons of rubber and caucho were received in Manaos from the State, inclusive of that in transit from Peru, Bolivia, and Venezuela. In 1909–10 this total had risen to 30,065 tons. This was natural or "wild" rubber, from vines and trees indigenous to the soil.

The Federated Malay States and Straits Settlements figure largely as present and prospective rubber producers. The quantity harvested practically doubles each year; in 1906 there were 1,035,601 pounds exported; in 1907, 1,989,889 pounds; in 1908, 3,186,099 pounds; in 1909, 6,112,023 pounds; and in 1910, 12,245,864 pounds. In view of the large acreages put under rubber during recent years, it is anticipated that equal increases will be shown in the future.

In 1842 and for many years all rubber was derived from wild plants, and the method of collecting it destroyed vast numbers of trees and vines, until it seemed probable that the supply of rubber would soon be exhausted. In 1876 Mr. Wickham was commissioned by the authorities at Kew Gardens to proceed to the Amazon Valley to secure a supply of Para rubber seeds. He brought back about 70,000 seeds, from which nearly 2,800 plants were raised at Kew Gardens and exported in miniature hot-houses to the Botanic Gardens at Ceylon. From these plants additional seeds were obtained. At the same time plants were introduced into Singapore, and seeds were sent from there to Borneo, Perak and elsewhere.

In 1884 tapping cultivated trees first took place in Ceylon, and in 1888 in Singapore, but not until 1899 was the first sheet rubber (from trees in Perak) sold in London—the first cultivated Para rubber placed upon the European markets. In considering these facts, one must be impressed with the rapid growth that has since taken place.

In Ceylon, for example, notwithstanding that thousands of acres are given over to tea, rubber cultivation is one of the most important planting industries. Although the island does not possess any indigenous rubber-yielding plants, the climate and soil have proved very suitable for the growth of Para, Ceara, and Castilloa rubber trees—the first named in particular. In 1900 it is stated that only 1,750 acres were under rubber in the whole island; but since then the development has been extremely rapid. In 1910 it was estimated that no less than 200,000 acres were planted with rubber.

The average cost of establishing a rubber plantation in Ceylon, and maintaining it up to the sixth year, is estimated at £25 ($121.66) per acre, apart from the cost of the land. Tapping can usually be commenced on trees 5 years old, and about 150 pounds per acre are obtainable in the seventh year, after which there is a considerable increase. Plantation rubber from Ceylon has, it is claimed, usually realized prices slightly in excess of those of fine Para from South America. The Ceara tree (at first unsatisfactory) can now be grown in situations in the island which are unsuitable for Para trees. When well prepared, Ceara rubber obtains prices equal to plantation rubber.

The growth of the rubber output of Ceylon is shown in the following statement: In 1903, $18^{1}/_{2}$ tons; 1904, $34^{1}/_{2}$ tons; 1905, 75 tons; 1906, 146 tons; 1907, 248 tons; 1908, 407 tons; 1909, 666 tons; 1910, 1,601 tons. The output for 1911 is estimated at 2,230 tons. It is thought a total crop of 30,000 tons will be realized in 1920.

British Guiana is being opened up and placed under the cultivation of rubber and balata. Of the latter over 1,000,000 pounds are annually exported, the demand for it continually increasing, especially in the United States. Licenses for its collection are issued for terms not exceeding 15 years, and the major portion of the easily accessible lands have been leased. As regards rubber, there are 9,000,000 acres of lands of easy access still unalienated and 36,000,000 of hilly lands; of this 45,000,000 of acres, a very large portion is stated to be suitable for rubber cultivation, the costs of which are low, it being possible to plant land at a cost of $68 per acre for the first year, with an annual expenditure of about $29 per acre in subsequent years.

Trinidad and Tobago are among the latest producers of rubber. The kinds most extensively grown are Hevea (Para) and Castilloa, while some Ceara and Funtumia are produced in the drier localities. It is stated that there are many thousands of acres in the southeastern part of the island suitable for rubber cultivation (of the two first-named varieties) which are not yet alienated, and which can be purchased by settlers at $12.25 per acre, survey included. The growth of the industry in Tobago is shown in the increase of the exports of rubber from 91 pounds in 1904 to 4,348 pounds in 1910, notwithstanding the fact that the trees are young and that only a small area has been tapped.

In recent years Dominica has been extensively planted with rubber—Hevea and Castilloa—and it is stated the growth is luxuriant, and results demonstrate that the islands are well suited for rubber cultivation. The Crown lands comprise about 100,000 acres, and are sold at $2.45 per acre. The payment for blocks exceeding 100 acres can, if desired, be spread over three or four years.

German as well as British East Africa is fast becoming a factor in the world's supply, together with Uganda, while in

Mexico tapping has been going for years. On one plantation (La Zacualpa) there are nearly 4,000,000 trees (of the Castilloa variety). This and a sister plantation showed live trees at the exhibition, from which demonstrations were given of tapping (or "milking") and collecting the latex which, by the use of centrifugal machines, can be converted into solid cones within half an hour. By this process, it is claimed that sheet rubber to suit the market is ready for shipment in three hours, as compared with three days by the ordinary method.

Although the total quantity of rubber exported from Uganda since 1902 has amounted to only 467,040 pounds, valued at $250,000, this was derived chiefly from vines. Ceara was introduced in 1902, and has been found a valuable addition to the country's resources. Three-year-old trees yield an average of 30 ounces of dry rubber per annum, while 8-year-old trees yield 19 ounces in $2^{1}/_{2}$ months. Tapping is on the "half herringbone" system, every alternate day, to a height of 4 feet. Para was introduced in 1901, and makes excellent growth; an 8-year-old tree attains a growth of 35 inches, and yielded $16^{1}/_{2}$ ounces of dry rubber in 107 tappings.

Castilloa and Manicoba plants are not recommended for Uganda, the former being subject to attack by a boring beetle and the latter slower in growth than Ceara. There are, it is stated, several rubber plantations in the country, and plants are making rapid and strong growth. The cost of land (freehold) is about 65 cents per acre.

In view of the growing output, which is due not only to the increasing acreage, but also to the fact that as trees develop they give a larger yield each year, it is held by some authorities that the time is approaching when the supply will exceed the demand. Shrewd judges, however, are not of this opinion, because new uses for rubber are constantly being found, and in their view there is a field for much further utilization. White rubber is now extensively used in surgical, medical, and scientific apparatus and appliances, household requisites, and to an enormous extent, for tires. In addition to many other ways, it has yet to be used as a paving in cities in a general direction. Although this use is not new, the chief drawbacks at present are its cost and the need of a perfected method of manufacture.

Samples of rubber paving were laid down in the exhibition by a British company; and recently banks and insurance companies and other large buildings have utilized it in this way. In the opinion of the president of the exhibition, "the problem had made great strides," and he "felt sure before long a process for the application of rubber to street paving would be perfected."

The exhibit of one of the American companies which attracted a good deal of attention was a miniature rubber factory demonstrating modern methods of using guayule rubber in various rubber goods on the market. The process of extraction of rubber from the shrub (a native of Mexico) was indicated by samples taken at different points of manipulation. First, it was shown how the rubber is washed and sheeted; then dried by a high vacuum and low-temperature method. The rubber is next put on the mixing mill, and can be easily worked to requirements. Guayule, it is claimed, is better than it looks. In appearance it is a "somewhat low, softish rubber," but vulcanizes remarkably. Blended with other rubber, it is practically suitable for any grade of goods, and is being used on a large scale. The estimated amount produced in 1910 was 28,500,000 pounds, of which this company produced 15,000,000 pounds. It is marked in a clean condition in bags weighing about 150 pounds. According to the company's statement, guayule is successfully employed in making all classes of belting, packing, hose, valves, mats, disks, and a thousand and one molded articles for all purposes, as well as entering into the composition of boots, shoes and tires.

An American rubber mill machinery manufacturing firm exhibited various machines in connection with the guayule miniature factory exhibit. The machines were not of full size, but were very complete.

In addition to the numberless kinds, classes, and grades of rubber shown, there were exhibits of coconuts, sisal hemp, oilseeds, catchcrop beans of various kinds (including soya beans from the British East African Protectorate), and kapok. The latter was exported from German East Africa and appeared to be of excellent quality. It is not, however, on the London market, but is shipped to Hamburg for sale and export.

In an interesting article written by Mr. Walter Freudenberg, of Bremen, the future supply of rubber is dealt with. He quotes the estimated planted acreages as given by three of the leading trade publications: India Rubber Trades Diary, 776,000 acres; India Rubber Journal, 980,000 acres; Gummi-Zeitung (Berlin), 1,310,000 acres; and he takes the second as a basis for future yields: From Malaya (authority, Sir John Anderson), 70,000 tons; Ceylon (authority, Ceylon Observer), 19,000 tons; Dutch Indies, Borneo, South Mora and Burma, 20,000 tons; total annual supply of plantation rubber in 1916–17, 109,000 tons. To this must be added the probable supply of wild rubber, which until recently has been about 70,000 tons annually. He considers, however, that the supply from this source may decrease, in view of the larger crop of plantation rubber, and estimates only 35,000 tons, making a gross total of 144,000 tons in 1916–17.

As to the present and probable future consumption, it would appear from available statistics that for the year ending June 30, 1910, a total of 76,000 tons was used, showing an increase of about 5 per cent. annually during the past 10 years; and if this rate of increase continues, about 107,000 tons would be required by 1916–17. But this rate of increase does not, of course, take into consideration new uses to which rubber may be put.

The imports of raw rubber by the United Kingdom, Germany, Belgium and the United States, the five principal users, for the first five months of 1911, and for the years 1909 and 1910, are shown in the following table (in long tons):

	First five months.	Twelve months.	
	1911. Tons.	1910. Tons.	1909. Tons.
United Kingdom	20,000	44,000	35,000
Germany	8,400	18,700	15,550
Belgium	4,570	10,550	8,550
France	9,020	19,980	15,220
United States[1]	28,773	87,352	60,312

NOTE.—This table should not be understood to represent the actual quantity of rubber produced in the years indicated, the figures including transshipments from one country to another.

UTILIZATION OF WASTE METALS.

Figures showing the recovery of "secondary" copper, lead, zinc, tin and antimony in the United States in 1910 are summarized by the Geological Survey in the table below. The secondary metals include those recovered from scrap metal, sweepings, drosses, etc. They are called "secondary" to distinguish them from the metals derived from ore, which are known as "primary" metals.

The table gives the quantity and value of each secondary metal recovered during the years 1909 and 1910. The large increase shown in the figures for 1910 was occasioned partly by increased business activity and the growing tendency toward conservation, but is explained in part by the fact that in 1910

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[1] Including balata, guayule, gutta-percha, gutta-jelutong, and scrap rubber.

the Survey made a more extensive canvass of the sources of production. As these secondary metals displace equal quantities of primary metal in supplying consumption, they undoubtedly affect the prices of primary metals to some extent now and will affect them even more in the future.

	1909.		1910.	
Metals.	Short tons.	Value.	Short tons.	Value.
Secondary copper, including that in alloys other than brass............	25,396	$6,602,960	51,000	$12,954,000
Remelted brass......	27,347	5,863,181	62,000	13,032,400
Secondary lead......	17,822	3,538,814	29,384	4,868,400
Recovered lead in alloys............	23,327		25,939	
Secondary spelter....	33,040	3,695,868	41,223	4,744,300
Recovered zinc in alloys other than brass............	1,181		2,709	
Secondary tin........	2,423	3,281,425	7,217	9,481,800
Recovered tin in alloys............	3,092		6,686	
Secondary antimony	27	257,362	9	444,600
Recovered antimony in alloys..........	1,529		2,770	
Total value.......	..	23,239,610	..	45,525,500

The total amount of secondary copper recovered, on the assumption that the brass remelted had an average copper content of 70 per cent., was 91,500 tons, of which 15,500 tons was recovered by regular refining plants and the remainder by plants treating only secondary material. At least 30,000 tons was recovered from clean scrap made in the course of manufacture of copper and brass ware, so that only 61,500 tons were obtained from ashes and cinders and from material that had entered the trade in manufactured form and been discarded. The Survey inquiry was extended so as to include the railway companies' figures for old metals reused by themselves, and to these is attributed a large proportion of the increase in the figures for copper. The production from secondary sources in 1910 was equal to about 17 per cent. of the domestic consumption of new copper.

The secondary lead was equal to 11.5 per cent. of the refined lead produced in the United States.

The secondary zinc (including that in brass) equals 23.2 per cent. of the total production as primary spelter in the United States.

The secondary antimony (recovered almost wholly in alloys) shows a large increase and, as the production from domestic antimonial lead ores was comparatively small, the secondary recoveries are the only important domestic source of supply.

The production of tin from ore mined in the United States is negligible, so that the secondary recoveries constitute practically the sole domestic supply. The figures for 1910 recoveries show a large increase over those for 1909, mainly because the quantity of metal recovered from scruff and drosses from tin and terne plate manufacturers was ascertained. There were also several plants which made tin oxide and tin chloride from clean scrap tin. The production of these compounds is calculated as metal to avoid disclosing the output of products having a limited use. Although a large quantity of tin is recovered from scrap by electrolytic treatment, and a smaller quantity is converted directly into oxide and chloride, the principal recovery is made from scruff and drosses, or in alloys.

THE WORLD HOP CROP.

Consul George Nicolas Ifft reports that statistics of the 1911 hop crop are now available, and while the crops in Bavaria and Bohemia, where the finest hops are grown, are only about half those of 1910, the figures show that the world's crop this year was only about 230,000 hundredweight less than that of last year. The area planted to hops in Bavaria was slightly less than last year, while in Bohemia it was practically the same, and in the world as a whole it was only a few hundred acres larger. Brewers who must have the prime Bavarian and Bohemian hops must this year pay high prices, shipments now (Sept. 29) being invoiced at from 70 to 80 cents per pound from Nuremberg; but on the whole there are no indications of a shortage in hop supply.

ACREAGE AND CROP OF THE WORLD.

The following tables give the area planted and total crop of the world for the last three years, the hundredweight used meaning bales of 50 kilos, or 110 pounds.

	Area planted.			Total crop.		
Countries.	1909. Acres.	1910. Acres.	1911. Acres.	1909. Cwt.	1910. Cwt.	1911. Cwt.
Germany.......	71,568	67,867	65,934	119,000	384,000	222,000
Austria-Hungary	58,148	52,194	51,826	164,000	297,000	178,000
France.........	6,920	6,920	6,920	27,000	54,000	45,000
Belgium and Netherlands...	5,204	4,793	4,942	29,000	58,000	52,000
Russia.........	20,786	22,407	22,240	60,000	58,000	62,000
England.......	32,565	32,911	34,595	205,000	296,000	354,000
America.......	43,635	44,478	46,950	310,000	400,000	400,000
Australia.......	1,853	1,828	1,828	10,000	10,000	15,000
Total	240,679	233,398	235,235	924,000	1,557,000	1,328,000

The figures for Germany and Austria-Hungary in the foregoing table are based upon complete and semiofficial reports from all hop-growing districts, and those for other countries upon very full reports received by one of the oldest and most reliable firms of hop dealers in this market, and they may be accepted as the best figures at this time obtainable.

RUSSIAN CROP ESTIMATES.

Consul John H. Grout submits a Russian trade journal estimate of the probable amount of grain to be expected in Russia this year. This estimate is based upon statistics gathered between the first and the middle of July last, and is given in the following table, together with the totals for 1910, and the average crop from 1906 to 1910:

Class of grain.	Average crop. 1906–1910. Tons.	1910. Tons.	1911. Tons.
Winter rye........................	21,280,600	23,839,200	22,154,400
Winter wheat.....................	5,839,200	7,437,600	5,839,200
Spring rye........................	496,800	376,200	291,600
Spring wheat.....................	12,218,400	15,757,200	12,979,800
Barley...........................	8,922,600	11,064,600	10,443,600
Buckwheat........................	1,126,800	1,346,400	984,600
Millet...........................	2,417,400	2,899,800	2,039,400
Maize............................	1,431,000	2,165,400	1,704,600
Oats.............................	14,833,800	16,684,200	14,689,800

Since the foregoing estimate was made, there has been considerable deterioration of the crops. It is possible that a reduction of something like 5 per cent. to 10 per cent. may safely be made in order to arrive at a reasonable estimate of the results of the 1911 crop. Aside from the matter of quantity, reports are arriving to the effect that quality has suffered as well, at least in many parts of the country.

PIG IRON PRODUCTION OF JAPAN.

Consul General Thomas Sammons reports that an estimate supplied by the Department of Finance places the production of iron in Japan for 1910 at 71,963 tons, valued at $1,410,685. The average production for the past 10 years has been 50,030 tons, valued at $1,010,529, but the output has been increasing, the figures for 1901 having been 32,455 tons, valued at $602,196.

During 1910 Japan imported pig iron to the extent of 117,227 tons, valued at $1,675,371, of which 98 per cent. came from Great Britain, and less than one-tenth of 1 per cent. from the United States. The remainder was divided between China, Sweden and Germany, in that order.

Japan also imports iron ores, 208,191 tons having been received in 1910, with a value of $579,819, of which China supplied 61 per cent., Korea 35 per cent., and Great Britain 3 per cent., the 1 per cent. remaining coming from other countries.

CANADA'S TIMBER RESOURCES.

An official publication of the Dominion forestry branch of the Department of the Interior says: "The original timber area, omitting semitreeless lands, was approximately 1,900,000 square miles; 98,000 square miles have been cleared for settlement, and 100,000 square miles have been cut over by lumbermen, leaving a timbered area yet untouched of 1,702,000 square miles. Assuming the average of 3,000 feet per acre, there should yet remain 3,279,000,000,000 feet of timber in Canada at a very conservative estimate. The highest estimate that has been made hitherto, that given by the conservation commission, places the amount of saw timber and pulp wood in Canada at 494,600,000,000 feet and 1,100,000,000 cords, respectively." The forest area of Canada has been variously estimated by experts from time to time, but the above figures seem to be the most accurate the Government ever issued on the subject.

CLAY-PRODUCTS EXPOSITION.

An exposition covering the clay-products industries will be held in Chicago, March 7 to 12, 1912, and the early plans promise the most complete display of the various lines comprised in this industry that ever has been provided.

At the time of the exposition there will be a number of conventions of organizations which are allied with the clay-products industries. Among those which, according to the Construction News, will meet at this time are the National Brick Manufacturers' Association, the National Paving Brick Manufacturers' Association, the Building Brick Association of America, the Clay Machinery Manufacturers' Association, the American Ceramic Society, the Illinois Clay Workers' Association, and the Middle West Clay Workers' Association.

BOOK REVIEWS.

Modern Industrial Chemistry. By H. Blücher. Translated from German by J. P. Millington. 779 pages. 15 full page illustrations; 25 pages advertisements. Gresham Publishing Co., London. D. Van Nostrand Co., New York. Price, $7.50 net.

This book is obviously not intended for use as a text-book, but is essentially, on account of the arrangement of material and range of subjects, a small reference encyclopedia.

Subjects are arranged in alphabetical order and the author has exercised a startling liberty in selecting material for discussion under the general title of Modern Industrial Chemistry. In this connection one is somewhat surprised to find space given to such subjects as Accidents, including directions for "Treatment of Frozen People," "Sunstroke," "Poisoning," etc. Granting that these are important directions to have within the reach of factory chemists, it is not likely they would think of looking in a volume on Industrial Chemistry for such emergency information. Artificial Diamonds (page 219) has been given almost a page, with no qualifications as to the commercial importance of this as an industry. The lack of a sense of proportion so common in works on Industrial Chemistry is one of the most conspicuous features of this book. Industries of little or no productive or typical value are discussed at length, while some of our greatest industrial propositions are dismissed with a paragraph or two. At least half of the material is general descriptive data, to be found in text-books on chemistry or physics.

Ambiguity is a conspicuous feature in many of the statements. It is doubtful if a clear conception of a filter-press would be established in any one's mind by reading this description (page 274): "A filter-press consists of a series of boxes between two strong head-pieces, one movable and one fixed (the latter on stand), resting on two strong side spindles and lined with some suitable filtering material." Again, the statement is made, under Cellulose (page 150): "Among the fiber substitutes used in the manufacture of paper, mechanical wood pulp and cellulose should be mentioned. For the former Cf-WOOD. Cellulose differs from wood pulp in that it is a pure chemical product free from impurities."

The subject of Cement is disposed of in less than two pages. The statements are so involved, and so far from representing the modern industrial practice, that it would be a calamity to have this fall into the hands of a student or one seeking general information on this important industry.

Under the heading of "Gaseous Fuels" (page 287), the author enumerates coal gas, oil gas, wood gas, producer gas, and acetylene. The reviewer is not familiar with the use of acetylene for fuel purposes, but recalls that millions of cubic feet of natural gas (not mentioned) are used annually.

Patents are frequently referred to by numbers and country, and the quantity of such references creates a doubt as to their real importance in the advancement of the industry under consideration. Frequent reference is also made in the notes, to advertisers who have taken space in the 25 pages of the book devoted to that purpose.

The reviewer is at a loss to determine just what is the purpose of such a book. The collection of an indiscriminate lot of general physical and chemical data, much of which is simple definition, compiled without regard to the commercial importance of the subject under discussion, with very few attempts to describe or illustrate the logical steps of manufacture, and arranged in alphabetical "illogicalness," is obviously unlikely to produce a book on Modern Industrial Chemistry. Such a book would have a doubtful value, either to the lay reader, the student, or works manager. A preface by the author or the translator might have suggested their views on this point, but we were denied this helpful suggestion, and instead favored with a monograph on the value of the work by the publisher.

M. C. WHITAKER.

Lubricating Oils, Fats and Greases. By GEORGE H. HURST. Third Edition. Revised and enlarged by Henry Leask. 390 pp. Scott, Greenwood & Son, London. D. Van Nostrand Company, New York. 1911. Price, $4.00.

This third edition of Hurst's well-known book, while enlarged and improved, retains in the main the characteristics of the two former editions. It deals with the subject as is natural, largely from the standpoint of the English user of oils: the description in Chapter III of the Scotch Shale Oil Industry is full, and is brought up to a recent date while Chapter IV on Petroleum, though sufficiently complete for the probable user of the work, takes little account of the more recently developed fields of petroleum and the products peculiar to them.

The chapter devoted to Vegetable and Mineral Oils and Fats gives a good general view of the subject although in many details, particularly in the statements of the "Constants of Oil," erroneous ideas would be derived by the casual reader, as for example, the statement of the specific gravity of each oil in the fourth place of decimals as though it were a fixed and unchanging characteristic of the particular oil in question. Something of the same fault may be found with the chapter on the Testing and Adulteration of Oils; it is not at all clear from the text that the analysis of a mixture of lubricating oils is of any different nature in the accuracy and certainty of the results of the analysis from the analysis of an ordinary rock or mineral.

On the whole the book is a useful one as a general treatise on the subject. PARKER C. MCILHINEY.

Wood Pulp and Its Uses. By C. F. CROSS, E. J. BEVAN AND R. W. SINDALL. 251 pages. 35 illustrations. D. Van Nostrand Company, New York. 1911. Price, $2.00.

The authors have given in this book a general account of the evolution of the wood pulp industry.

As is to be expected, in covering a field as large as the uses of wood pulp, and presenting it both to the technical and general public, certain sections, as Chapter II, reproduced in part from the "Researches on Cellulose," is too technical for the latter. The authors indicate in the preface that they do not intend the book to be an exhaustive text-book of the subject; this explains why certain other sections are not more elaborated.

The work is divided into eleven chapters, as follows:

Chapter I: The Structural Elements of Wood.

Chapter II: First, Cellulose as a Chemical Individual and Typical Colloid. Second, The Lignone Complex, Lignocellulose; Special Chemical Note on Autoxidation, and Researches of W. J. Russell.

Chapter III: Wood Pulps in Relation to Sources of Supply: Forest Trees and Forestry.

Chapter IV: The Manufacture of Mechanical Wood Pulp.

Chapter V: Chemical Wood Pulp.

Chapter VI: News and Printings.

Chapter VII: Wood Pulp Boards.

Chapter VIII: The Utilization of Wood Waste.

Chapter IX: Testing of Wood Pulp for Moisture.

Chapter X: Wood Pulp and the Textile Industries.

Chapter XI: Specimen Pages.—Various Types of Paper. This chapter consists of eleven specimen papers of varying composition, giving complete data as to strength, weight, loading, size, etc.

A bibliography has also been included, which gives the character of subject matter of each book. Many of the calculations as to cost, power consumption, statistics, etc., are of course based upon the English system and practice.

The authors have succeeded in producing an instructive book on the numerous uses of wood pulp and waste wood, which is certain to be of interest to the general public and the manufacturers of wood pulp and wood pulp articles. O. KRESS.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

Agricultural Chemistry, Yearbook on the Advances in—. By T. DIETRICH. Vol. XIII. L. 8vo., 619 pp. $5.50. Berlin, 1911. (German.)

Albuminoids, Chemistry of the—. By O. COHNHEIM. 3d Ed. 8vo. $3.00. F. Vieweg & Sohn, Brunswick. (German.)

Alloys, Composition of the Commoner—. By N. KAISER. L. 8vo., 26 pp. $0.75. Halle, 1911. (German.)

Analysis, The— and Examination of Agriculturally and Technically Important Substances. By J. KOENIG. 4th Ed. 8vo. $9.00. Berlin, 1911. (German.)

Analysis, Handbook of Organic—. By H. T. CLARKE. 8vo., 272 pp. $1.25. London, 1911.

Analysis, New Reduction Methods in Volumetric—. By E. KNECHT AND E. HIBBERT. 8vo. $1.25. New York, 1911.

Analysis, Technical Methods of Chemical—. By GEORGE LUNGE. Vol. II. Translation. 8vo., 1294 pp. $15.75. Gurney & Jackson, London.

Analysis, The Technical— of Brass and the Non-ferrous Alloys. By W. B. PRICE AND R. K. MEADE. 12mo., 267 pp. $2.00. John Wiley & Sons, New York.

Analytical Chemistry, The Indirect Methods of—. By J. Fages y Virgili. 8vo. $1.00. F. Enke, Stuttgart. (German.)

Analytical Chemistry. By F. P. Treadwell. Translation. Vol. II: Quantitative Analysis. 3d Ed. 8vo., 903 pp. $4.00. John Wiley & Sons, New York.

Biochemical Dictionary. By E. Abderhalden. L. 8vo., 1499 pp. $23.00. Vol. I. Berlin, 1911. (German.)

Bricks, Handbook of the Manufacture of—. By K. Duemmler. Part I. L. 8vo., 32 pp. $2.00. Halle, 1911. (German.)

Calorimetric Methods. By W. Glikin. 8vo., 210 pp. $3.00. Gebr. Börntraeger, Berlin. (German.)

Carbon, Mineralogy of—, or Organic Mineralogy. By K. W. Charitschkow. 8vo., 240 pp. $1.75. Tiflis, 1911. (Russian.)

Cement, Manufacture of—. By J. Fritsch. L. 8vo., 503 pp. $5.00. Paris, 1911. (French.)

Chemicals, A Dictionary of— and Raw Products Used in the Manufacture of Paints, Colors, Varnishes, etc. By George H. Hurst. Demy 8vo., 380 pp. $2.25. Scott, Greenwood & Co., London.

Chemical and Microscopical Diagnosis. By F. C. Wood. 3d Ed. 8vo., 791 pp. $5.00. D. Appleton & Co., New York.

Chemotherapy, Theory and Practice of—. By Paul Ehrlich. 8vo., 28 pp. W. Klinkhardt, Leipzig. (German.)

Chemistry, Modern Science Reader with Special Reference to—. By Robert B. Bird. 12mo. $1.10. The Macmillan Co., New York.

Chemistry, Treatise on—. By H. E. Roscoe and C. Schorlemmer. 4th Ed., Vol. I. Roy. 8vo. $5.50. London, 1911.

Chemistry, Yearbook of—. By R. Meyer. Vol. XX. L. 8vo., 568 pp. $4.50. Brunswick, 1911. (German.)

Concrete, Reinforced—. By P. Rohland. 8vo. $0.75. Otto Spamer, Leipzig. (German.)

Electrochemistry, Applied—. By M. de K. Thompson. 8vo., $2.10. The Macmillan Co., New York.

Electrochemistry. By Max Le Blanc. 5th Ed. 8vo. $1.75. Oskar Leiner, Leipzig. (German.)

Electrolytic, Examples for the— Production of Chemical Substances. By K. Elbs. 2d Ed. 8vo. $1.50. W. Knapp, Halle. (German.)

Foods and Drugs. By E. J. Parry. 2 Vols. Roy. 8vo., 904 pp. $7.50. Scott, Greenwood & Co., London.

Food Materials, Handbook of the Analysis of—. By C. U. Dahle. 8vo., 120 pp. $1.00. Christiania, 1911. (Norwegian.)

Gas, The Construction and Management of Small— Works. By N. H. Humphreys. 8vo., 268 pp. $2.00. J. Allan & Co., London.

Gliadin, Some Factors Influencing the Quantitative Determination of—. (Proteid of Wheat.) By J. E. Greaves. Roy. 8vo., 44 pp. Berkeley, 1911.

Hydraulics, A Treatise on—. By Hector J. Hughes and Arthur T. Safford. 8vo. $3.75. The Macmillan Co., New York.

Industrial Chemistry, Modern—. By F. J. G. Beltzer. 2 Vols. L. 8vo., 1526 pp. $8.25. Paris, 1911. (French.)

Inorganic Chemistry, Outlines of—. By E. B. Ludlam. 8vo., 382 pp. $1.25. London, 1911.

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

Acids: The Consumption of the Commoner— in the United States. By Charles E. Munroe. *Journal of the Washington Academy of Sciences*, Vol. I, No. 3, pp. 70–73.

Beer: What are the Causes of the Precipitation of Albuminoids in Finished Bottled—. By F. Emslander. *Letters on Brewing*, Oct., 1911, pp. 12–18.

Cacao: Test for Hulls in— and in Cacao Preparations. By Chr. Ulrich. *Archiv der Pharmazie*, 1911, No. 7, pp. 524–560.

Cellulose: Viscosity of— Solutions. By H. Ost. *Zeitschrift fuer angewandte Chemie*, 1911, No. 40, pp. 1892–1896.

Champaca Oil. By Benjamin T. Brooks. *Journal of the American Chemical Society*, November, 1911, pp. 1763–1772.

Coco-nut Oil. By E. Bontoux. *Seifenfabrikant*, 1911, No. 42, pp. 1045–1046.

Coking: The Chemistry of the— Process. By W. Hempel and F. Lierg. *Zeitschrift fuer angewandte Chemie*, 1911, Heft, 43 pp. 2044–2046.

Electroanalysis: The Use of the New Edison Storage Battery in—. By O. Brunck. *Zeitschrift fuer angewandte Chemie*, 1911, Heft 42, pp. 1993–1997.

Elements: Distribution of the Chemical— in the Terrestrial Shell. By V. I. Vernadskii. *Bulletin of the Imperial Academy of Sciences of St. Petersburg*, 1911, No. 14, pp. 1007–1018.

Elements: Concerning a New Arrangement of the— on a Helix, and the Relationship which May be Usefully Expressed thereon. By B. K. Emerson. *Science*, Nov. 10, 1911, pp. 640–652.

Tar and Tar Products. By A. D. Whittaker. *Progressive Age*, Nov. 1, 1911, pp. 915–918.

Gas: Some Principals of Condensation with Especial Reference to Water—. By L. E. Worthing. *Progressive Age*, Nov. 1, 1911, pp. 911–914.

Fatty Acids: Determination of Free— in Fats in the Presence of Alkaline and Earthy-alkaline Soaps. By D. Holde and J. Marcusson. *Zeitschrift fuer angewandte Chemie*, 1911, Heft 41, pp. 1945–1946.

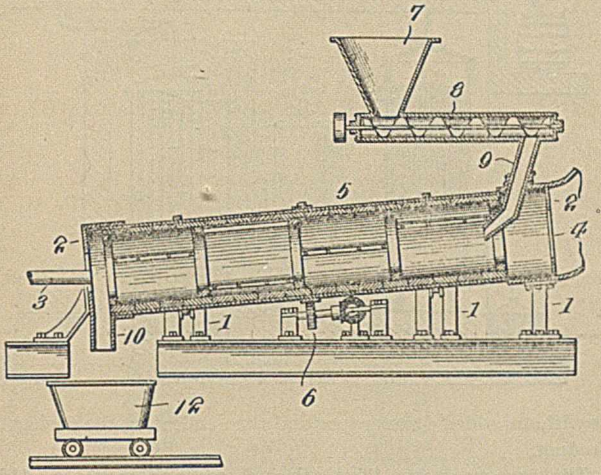
RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, Washington, D. C.

PROCESS OF MAKING PENTOXID OF PHOSPHORUS FROM CALCIUM SILICATE.

U. S. Patent No. 997,086, to S. Peacock, Chicago, assignor to American Cyanamid Company, New York.

A process of making the pentoxid of phosphorus from phosphate rock, or other source of cheap phosphate of lime and silica.



The accompanying illustration shows a type of furnace suitable for carrying out this process. Mixtures of phosphate of lime and silica or silicious clays are proportioned in accordance with the following reactions:

$$3Al_2O_3.3SiO_2.6CaO.2P_2O_5 = 3Al_2Ca_4.3SiCaO_3.2P_2O_5.$$
$$3SiO_2Ca_3(PO_4)_2 = P_2O_5.3CaSiO_3$$
$$3Al_2O_3Ca_3(PO_4) = P_2O_5.3CaAl_2O_4$$
$$3Fe_2O_3Ca(PO_4) = P_2O_5.3CaFe_2O_4.$$

The mixture of phosphate of lime and silica are proportioned in compliance with the reactions suggested, the whole is finely pulverized, mixed and passed through and heated in the furnace to about 1400° C. The phosphorus pentoxid is expelled by volatilization, and is absorbed in water, condensed or used as an acid upon fresh quantities of phosphate rock.

The usefulness of this invention depends upon the production of phosphorus pentoxid free from sulfuric acid, arsenic, antimony, or lower oxids, or phosphorus more or less poisonous or unsuitable for use in plant foods.

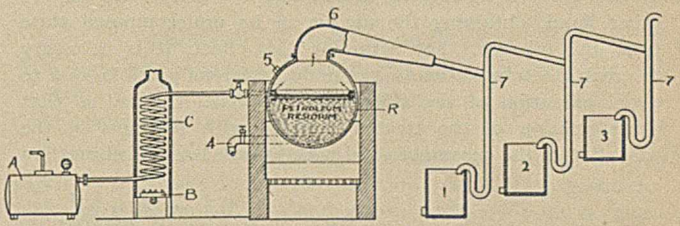
PROCESS FOR THE ANUFACTURE OF ASPHALT.

U. S. Patent No. 998,569, to C. B. Forward, Urbana, Ill.

A process for the manufacture of asphalt from petroleum residuum or from crude petroleum from which the lighter oils have been removed.

In handling the crude oil, or residuum, in a commercial way for the production of asphalt, the patentee first tries out a small quantity, about a gallon, in an open vessel at a temperature of about 625° F. The point to be observed is to keep it below the cooking temperature which destroys the value of the resultant product. The lighter oils can be removed much more rapidly in an open vessel than in a closed retort or still.

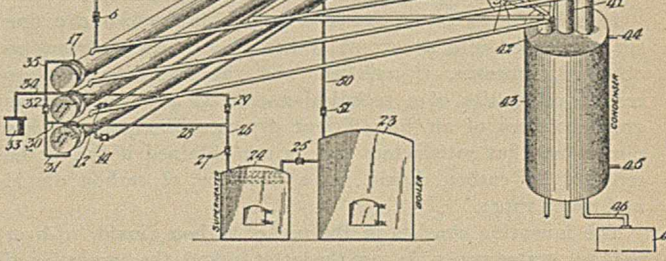
The patentee proceeds on a commercial scale in the following manner: The petroleum residuum is placed in a retort indicated by R in the accompanying drawings. If there be considerable moisture in the stock, it is subjected to a temperature of about 175° F. The moisture will precipitate as water, and can be drawn off from the bottom of the retort through an opening, 4. If there is but a small amount of moisture present, the temperature is put up to 240° to 250° F. and evaporated. If the temperature rises to 400° or 500° F. before the moisture has been removed, the residuum will foam. After the moisture is driven off the temperature is increased to 625° F. for a period of 24, 48, or even 60 hours, according to the gravity of the residuum. The exact time of subjecting it to the temperature of 625° F. has to be determined in each by experiment with the residuums of different gravities. After 36 to 48 hours at this temperature the resultant material in the retort is tested by withdrawing a small quantity through a suitable opening, as indicated at 5, and checks up at the same time the same quantity of distillate which has been taken off. When the product has acquired the desired consistency the material is transferred to an open vessel, and subjected to a temperature of about 100° F. less than it was in the still, for 5 to 20 hours, according to the product desired.



PROCESS OF REFINING OIL.

U. S. Patent No. 998,837, to Hubert G. Burrows, of Orcutt, California.

This invention relates to the treatment of crude oil containing a large amount of mineral matter in suspension, for example, crude oil which is obtained in Santa Barbara county, California, and which is found to contain mineral matter in the form of infusorial earth, in a state of such fine division that it remains permanently suspended in the oil and cannot be separated therefrom by the usual settling process on account of the viscosity of the oil.



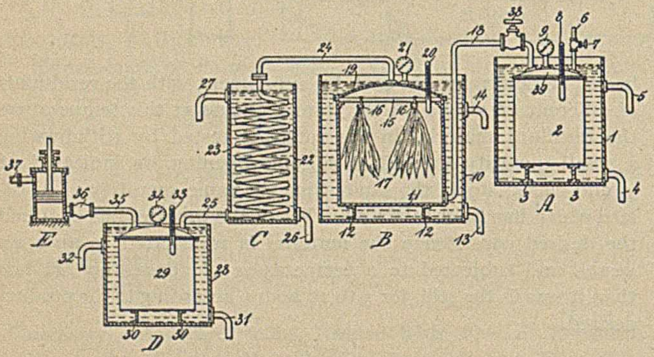
The object of the invention is to provide for effective separation of such mineral matter from the oil. The patentee discovered that by distillation of such oil under proper conditions, finely divided mineral matter will be carried over with the distillate, and, owing to the relatively small viscosity of the distillate, the mineral matter can be separated therefrom by the usual settling operation.

The accompanying illustration shows apparatus in which the process can be advantageously carried out.

METHOD OF REMOVING NICOTIN FROM TOBACCO.

U. S. Patent No. 999,674, to Johannes Sartig, of Nikolassee, near Berlin.

This invention consists in a new method of removing nicotin from tobacco while preserving as much as possible the quality of the tobacco as regards aroma and elasticity, and on the other hand, obtaining the nicotin in its undecomposed state from the tobacco. For attaining this effect, it is necessary to treat the tobacco at as low temperature as possible, and to avoid oxidation of the substances contained therein, so that contamination of the treated tobacco with products of the oxidation of the substances and with so-called resinified matters is rendered impossible, while at the same time the nicotin removed from the tobacco is recovered in its undecomposed state.



The method consists in treating the tobacco or tobacco products in closed vessels, where the air is rarefied, with low pressure steam at any temperature below 100° centigrade, while simultaneously preventing condensation of the steam in the tobacco by heating the closed vessels from without with surrounding liquid, and in conducting the volatilized nicotin with the steam, carrying it away to devices of any known construction for recovering the nicotin.

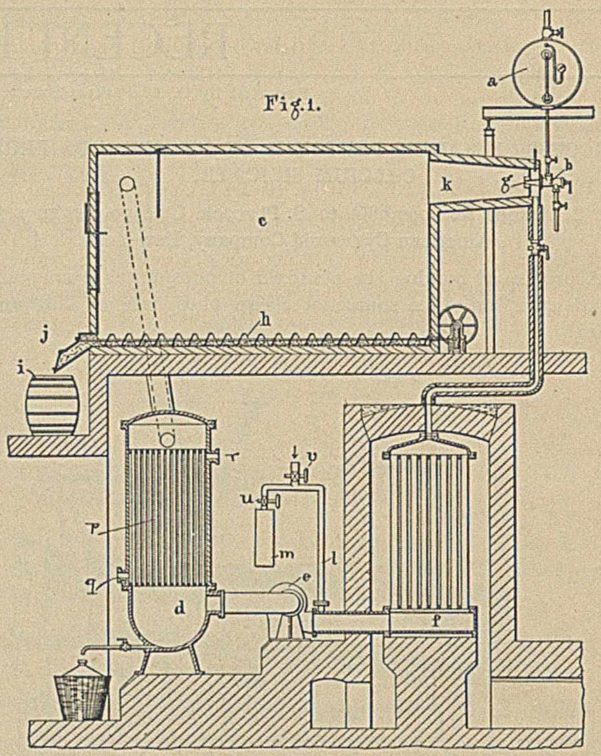
The accompanying illustration shows apparatus in which the process may be carried out.

DESICCATING MILK.

U. S. Patent No. 999,972, to Martin Ekenberg, London. Assignor to Techno-Chemical Laboratories, Limited, of London.

It is known that milk can be desiccated in the form of a fine spray injected into a current of heated air. The product so obtained, however, is oxidized, and the operation involves certain difficulties of a technical nature as a result of using great volumes of air for efficient drying. The patentee has discovered that satisfactory results are obtained if the air be replaced by carbon dioxid or a mixture of carbon dioxid and water vapor.

The invention consists in the use of carbon dioxid, with or without water vapor (in case the latter is used, the proportion of carbon dioxid to the same preferably not exceeding 6 to 1 by volume for the desiccation of milk and milk preparations) as by spraying the liquid or passing it in a finely divided form by, or into a heated current of dry or moist carbon dioxid with or without added water vapor and then collecting the desiccated product.



The accompanying illustration shows apparatus in which the process can be advantageously carried out.

APPARATUS FOR EXTRACTING METALS FROM THEIR ORES.

U.S. Patent No. 1,001,449, to J. H. Robertson, New York. Assigned to Universal Ore Reduction Company, of Phoenix, Arizona.

This is a method of electrically extracting a metal from a solution containing powdered ore. The continuous circulation of the solution between two conducting surfaces establishes an electrical current which causes the pure metal to be deposited

Fig. 1.

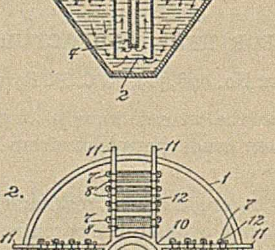
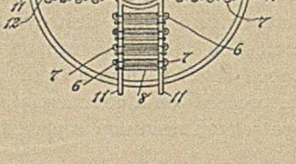


Fig. 2.



upon one of the surfaces, permitting the tailings to remain in the solution.

The process is carried out by apparatus shown in the accompanying illustration.

PROCESS FOR REFINING AND DESILVERING LEAD.

U. S. Patent No. 1,001,525, to G. P. Hulst, Omaha.

A method of refining and desilverizing impure lead bullion, which consists in melting the impure lead bullion, crystallizing a portion of the lead from the molten bullion by cooling and agitation and separating the molten impure lead from the crystallized lead by mechanical pressure applied to the crystals, the impure lead being conducted away from the crystals.

Fig. 2

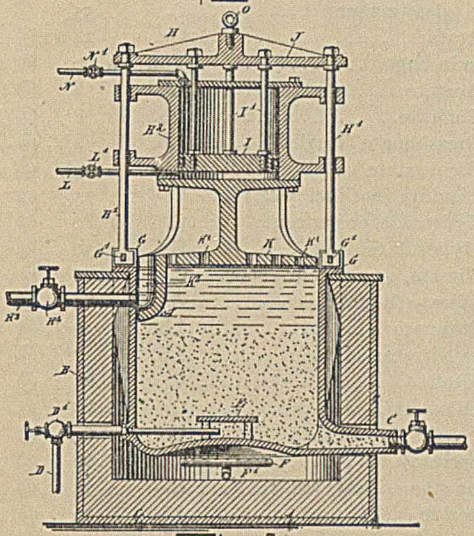
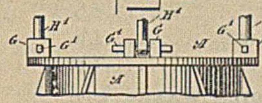


Fig. 3

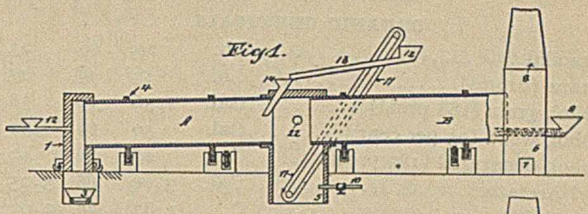


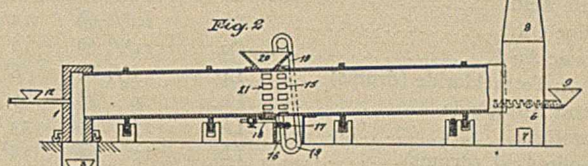
PROCESS OF MAKING CEMENT.

U. S. Patent No. 1,001,582, to Carleton Ellis, of Larchmont, New York. Assignor to Ellis-Foster Company, a Corporation of New Jersey.

This is a process of making cement clinker, which consists in crushing cement raw material to a coarse granular form, calcining the granulated material as a traveling stream, adding to the calcines a quantity of water, sufficient to substantially cool said calcines but insufficient to materially slake them, in regrinding the cooled calcines and clinkering the reground material, said process being conducted throughout in a continuous and non-cumulative manner.

The accompanying illustration shows apparatus in which the process can be carried out.

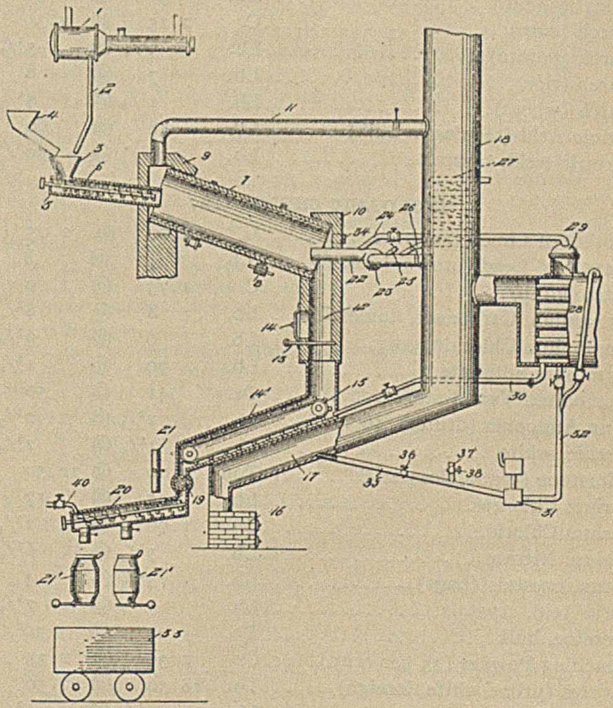




PROCESS OF MAKING ACETATES.

U. S. Patent No. 1,002,034, to H. O. Chute, Cleveland, and K. P. McElroy, Washington, D. C. Assignors to Ligno-Chemical Company, New York.

This is a method of preparing acetates from products of the digestion of woody fibers with alkali by heating such products under regulated conditions, and in recovering both the acetate formed, and the excess of alkaline reagent.



An alkali solution is produced, consisting of woody fiber constituents, the same being absorbed by a material capable of doing so. The mass is oxidized while in a heated state by diluted air, carbonizing by a higher heat out of contact with air, and separating the carbonate and acetate of alkali from the carbonized mass.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF NOVEMBER.)

Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	13¾	@	15
Alcohol, grain (188 proof)	Gal.	2.56	@	2.58
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	3.00	@	3.25
Acetic Acid	C.	1.87½	@	2.02½
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Oz.	11¼	@	12
Carbon Tetrachloride (drums)	Lb.	7¾	@	8¼
Carbon Bisulphide	Lb.	5	@	7
Chloroform	Lb.	27	@	33
Carbolic Acid (drums)	Lb.	17	@	18⅔
Citric Acid (domestic)	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.			44½
Dextrine (imported potato)	Lb.	6¼	@	7¼
Dextrine (corn)	C.	2.87	@	3.03
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19½	@	20
Iodoform	Lb.	2.95	@	3.00
Oxalic Acid	C.	7¼	@	7½
Pyrogallic Acid (bulk)	Lb.	1.25	@	1.55
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.15	@	2.30
Starch (potato)	Lb.	5¼	@	5½
Starch (rice)	Lb.	7	@	8
Starch (wheat)	Lb.	4⅞	@	5¼
Tannic Acid (regular in bulk)	Lb.	58	@	60
Tartaric Acid, crystals	Lb.	30¼	@	30¾

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.00	@	2.05
Acetate of Lead (brown, broken)	Lb.	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8¾
Ammonium Chloride, gray	Lb.	6	@	6¼
Aluminum Sulphate	Lb.	90	@	1¾
Ammonium Vanadiate	Oz.	41	@	50
Aqua Ammonia (drums) 16°	Lb.	2½	@	2½
Arsenic, white	Lb.	2⅜	@	2⅝
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chlorate	Lb.	15	@	17
Barium Chloride	C.	1.90	@	2¼
Barium Nitrate	Lb.	5½	@	6¼
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals	Lb	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.30	@	1.35
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	4½	@	4¾
Calcium Chloride	C.	65	@	90
Calomel, American	Lb.	94	@	96
Chalk (light precipitated)	Lb.	4½	@	6
Cobalt Oxide	Lb.	80	@	1.00
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bags)	C.	60	@	85
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Hydrochloric Acid (22°)	C.	1.45	@	1.75
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8	@	8⅝
Lithium Carbonate	Lb.	57	@	60
Magnesite (raw)	Ton	10.00	@	11.00
Mercuric Chloride	Lb.	85	@	88
Nitric Acid, 36°	Lb.	3⅝	@	4½
Nitric Acid, 42°	Lb.	4⅞	@	5¼
Phosphorus	Lb.	45	@	1.00
Phosphoric Acid, s. g. 1.75	Lb.	21	@	25
Plaster of Paris	C.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9⅜	@	10¾
Potassium Cyanide (bulk)	Lb.	20	@	24
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals,	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4⅛	@	4⅞
Potassium Bichromate, 50°	Lb.	7⅜	@	7¾
Pumice Stone	Lb.	2	@	4
Quicksilver	Lb.	63½	@	65½
Salt Cake (glass-makers)	C.	55	@	65
Silver Nitrate	Oz.	34	@	36
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4	@	4½
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5⅝	@	5¾
Sodium Bisulfite (not incl. pkg.)	C.	75	@	1.37½
Sodium Hydroxide, 60 per cent	C.	1.80	@	1.85
Sodium Hyposulfite	C.	1.30	@	1.50
Sodium Nitrate, 95 per cent., spot	C.	2.22½	@	2.25
Sodium Silicate (liquid)	C.	65	@	1.50
Sodium Stannate	Lb.	9¾	@	10
Strontium Nitrate	Lb.	7¼	@	8
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	12	@	12
Tin Oxide	Lb.	45	@	47
Tin Chloride (36°)	Lb.	11	@	11½
Zinc Chloride (granulated)	Lb.	4½	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	45
Black Mineral Oil, 29 Gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	10	@	11
Ceresin (yellow)	Lb.	9	@	20
Corn Oil	C.	6.30	@	6.35
Cottonseed Oil (crude), f. o. b. mill	Gal.	33	@	33½
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	8½	@	8¾
Lard Oil (prime winter)	Gal.	82	@	85
Linseed Oil (double-boiled)	Gal.	87	@	88
Paraffine Oil (high viscosity)	Gal.	23½	@	24
Paraffine (crude 120 @ 122 m. p.	Lb.	3	@	3⅛
Rosin Oil (first run)	Gal.	36	@	50
Spindle Oil, No. 1	Gal.	14	@	14½
Sperm Oil (bleached winter) 38°	Gal.	76	@	78
Stearic Acid (double-pressed)	Lb.	10¼	@	10½
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum [No. 1 ingots]	Lb.	18½	@	19
Antimony (Hallet's)	Lb.	7.50	@	7.85
Bismuth (London)	Lb.	—	@	1.80
Copper (electrolytic)	Lb.	12.25	@	12.35
Copper (lake)	Lb.	12½	@	12⅝
Lead, N. Y	Lb.	4.20	@	4.25
Nickel	Lb.	40	@	50
Platinum (refined)	Oz.	48.50	@	49.00
Silver	Oz.	54	@	55
Tin	Lb.	—	@	42
Zinc	Lb.	6.15	@	6.25