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THE PURIFICATION AND SOFTENING OF WATER BY PERMUTITE.

The advantages to be gained by the use of soft water in steam raising and for many manufacturing operations are now generally recognized. It is also conceded that the presence of iron in water for dyeing, printing, bleaching works and paper factories, is very undesirable. In brewing, too, water containing much iron is objectionable. Therefore, the application of the product "Permutite," an artificial zeolite, $3SiO_2.Al_2O_3(K_2O.Na_2O.CaO).6H_2O$, for the purpose of removing certain constituents from water and softening it, is of great interest to the chemist and engineer.

The Permutit-Filter Co., of Berlin, was organized in 1909 for the purpose of exploiting the above-mentioned artificial zeolite under the trade name "Permutite" (see Appelius, *Chem. Rev. Fett-Harz. Ind.*, **1909**, p. 300). This company devised also a process for softening water and for relieving it of iron and manganese (English Patent 26,074, Nov. 9, 1910). A number of other foreign companies are now being organized for developing these methods of water treatment. The "Permutite" process has been operated on a commercial scale at Glogau for the removal of manganese from water.

R. Gans (*Mitt. aus. d. Koenigl. Prufungsanst. f. Wasserversorgung u. Abwasserbeseitigung zu Berlin*, **1907**, p. 8; *Woch. f. Brau.*, **24**, 270) found that the aluminate-silicates exchanged their bases not only for alkalies and alkaline earths, but also for iron, manganese, lead, silver, and presumably for all metals. He pointed out that a filter of such material could be regenerated after use by washing with alkali salts, by which the metals separated from the water were redissolved. According to Gans, by fusing aluminum silicates with sodium carbonate and sufficient quartz to decompose all the carbonate, aluminate-silicates containing 12–15 per cent. Na_2O are obtained which are excellent filtering media. He stated that the soda content was of the greatest importance, since it was found to replace the bases present in the water. In one experiment conducted by Gans, well water which rapidly became turbid in the air, owing to the separation of iron, was filtered through a 10 cm. layer of calcium aluminate, the water level falling 10 cm. per hour. The whole of the iron was removed from the water by the filter, from which it was afterwards dissolved by washing with sodium chloride solution.

Gans also made experiments on the softening of water for boiler-feed purposes. A hard water was treated with sodium aluminate-silicate, which was found to remove the lime and magnesia quantitatively, leaving only the alkali carbonates, sulphates and chlorides, together with the small proportion of silicates contained in the original water. He found that if only three-fourths of the sodium of the sodium aluminum silicate was replaceable, 4.5 lbs. of the material would remove from 30 cu. ft. of water possessing a hardness of 20 degrees (German), all salts capable of forming boiler incrustation. Gans reported (*Chem. Ztg.*, **31**, 355) that manganese could be separated from water by filtration through a layer of granular aluminum silicate, prepared by fusing clay with an alkali carbonate, and adding to the fused mass sufficient quartz to combine with almost the whole of the alkali. After extracting the mass with water, the silicate was obtained in a granular or flaky form. Regeneration of foul filtering layers was found to be accomplished by washing with calcium chloride or calcium-sodium chloride solution. Gans also reported that hydrated silicates, both natural and artificial, were capable of withdrawing the bases from alkaline and neutral salt solutions, and that potash and soda might be eliminated from sugar juice by means of aluminun silicate (*Z. Ver. Deut. Zuckerind.*, **1907**, p. 206). In German Patent 174,097, of January 12, 1905, issued to Gans, it is pointed out that artificial zeolites or alkaline-earth aluminate-silicates for the purification of molasses need to be free from uncombined lime (see also French Patent 374,525, February 11, 1907, of the J. D. Riedel A.-G.; and United States Patent 943,535, December 4, 1909, of R. Gans, for the manufacture of hydrated aluminum silicates).

In a patent issued to Gans in 1907 (English Patent 8232, April 9, 1907) the claim is made for the manufacture of hydrated alumino-silicates, or artificial zeolites. About this time Gans gave further evidence of the usefulness of aluminum silicates for improving water supplies (*J. Gasbeleucht.*, **50**, 1026); he pointed out that iron and manganese were removed completely by passing the water through a filter composed of calcium-aluminum silicate; that a hard water could be softened by filtration through sodium-aluminum silicate, the latter material also serving to remove any iron, manganese and ammonia which might be present in the water; and recommended that in supplies where the hardness was due principally to calcium sulphate, the water be passed successively through layers consisting of strontium-aluminum silicate and calcium-aluminum silicate.

In 1908, Lührig and Becker (*Chem. Ztg.*, **32**, 514, 531) conducted experiments on the efficiency of the "Gans method" for removing manganese sulphate from water by means of natural or artificial zeolites. They found that similar results were obtained with the natural and artificial substances, but that the latter were more active; that a given quantity of manganese sulphate was most effectively removed from dilute solution made to filter slowly through a bed of the silicate; that the presence of the salts of other bases in solution was unfavorable to the absorption of manganese; and that by subsequent treatment of the silicate with solutions of salts such as ammonium chloride, in order to revivify it, the whole of the absorbed manganese was not removed, but was found to be present partly as hydrated peroxide, which, on a large scale, tended to obstruct the filter beds.

The patents granted to R. Gans and the J. D. Riedel A.-G. in 1909 (French Patent 405,990, July 17, 1909; English Patent 21,184, Sept. 16, 1909; and U. S. Patent 951,641, March 8, 1910) contain claims for a process for removing iron and micro-organisms from water. It is stated that the process consists in treating the water with insoluble higher oxides of manganese with the coöperation of natural or artificial zeolites (cf. German Patents 145,797 and 154,792). The claim is made that if a calcium-zeolite is treated with a solution of a manganous salt, a manganese zeolite is formed, which, on treatment with a solution of calcium permanganate, yields a product consisting of the higher oxides of manganese distributed in a fine state of division throughout a calcium-zeolite. According to Gans (*Chem. Ind.*, **32**, 197), 450 kg. of calcium-zeolite were found to be changed, by washing with manganous chloride solution, to manganese-zeolite; treatment with a calcium manganate solution converted the latter into calcium-zeolite again. On filtering the water to be treated through this material, the iron is said to be rapidly oxidized and removed, and the bacteria and organic matter destroyed; any manganese present in the water is also said to be removed. In later patents to the same parties (French Patent 409,006, Nov. 13, 1909; English Patent 26,842, Nov. 18, 1909; and U. S. Patent 960,887, June 7, 1910), the water to be softened is treated with barium, calcium or magnesium hydroxide, and sodium hydroxide or carbonate, according to the nature of the hardness, and then filtered through a layer of a natural or artificial zeolite.

When a water containing manganese salts in solution is passed through a filtering bed composed of a zeolite impregnated with higher oxides of manganese the manganese is separated in the form of a mud. It was found in practice as early as 1907 that if this mud was not removed from the filter, it eventually formed small porous particles which did not interfere with the filtering capacity of the bed, but, in fact, increased its efficacy with regard to the removal of manganese from water (see German Patent 220,609, Oct. 28, 1908, of the J. D. Riedel A.-G). However, when revivification was attempted—*i. e.*, on the bed containing manganese mud—the manganese retained was found to be an obstruction to rapid filtration.

Natural stones, such as trass, phonolite, porphyry, leucite, trachyte, sodalite, and mica, are also employed in making filters through which the water to be treated is passed. These minerals are used either directly, if they have been hydrated naturally, or after they have been treated with steam under pressure; but we are not aware of their application in the place of artificial zeolite.

Two investigations have recently been published on "Permutite." Anders (*Woch. f. Brau.*, **28**, 78) conducted laboratory experiments with the product for the softening of water. His results showed that "Permutite" is applicable for the softening of feed-waters, but not for mash-waters because it takes up sodium salts. He found that a "Permutite" filter may be completely regenerated by the use of a sodium chloride solution. Kolb (*Chem. Ztg.*, **35**, 1393, 1410) also investigated the application of "Permutite" to the softening, as well as the purification, of water. He made experiments, both by shaking and by filtration, as to the interchange occurring between "Permutite" and the chlorides of calcium, magnesium, and potassium, and found that the soda of the "Permutite" was replaced by the bases of the salts added in molecular proportions. He also ascertained that the "Permutite" could be regenerated by treating the used substance with sodium chloride, and that iron and manganese, as well as the alkaline earth metals, could be removed from solution. Kolb stated that with a filter formed of "Permutite," complete softening of water could be effected, but the water must not contain acid or suspended matter. In the case of a muddy water, in addition to blocking the pores of the filter, the mud coated the grains of the filtering material with inert matter and prevented the desired chemical reactions. Kolb considered the regeneration of the "Permutite" by a solution of sodium chloride to be of industrial importance, since it would enable the same filter to be used for an indefinite period. According to his findings, the richness of the treated water in sodium salts is not detrimental to boiler-feed water.

It would seem that "Permutite," to be of value for technical uses, must be of a granular or leafy, easily porous character, such as is obtained by melting together the constituents in definite proportions. The amount of clay is calculated according to the amount of bases. Gans considers that the composition of an ideal zeolite, $2SiO_2.Al_2O_3.Na_2O.6H_2O$, should be approached.

W. A. HAMOR.

THE PAINT AND VARNISH INDUSTRY OF THE UNITED STATES.

Up to ten years ago this industry was more or less in an empirical state. Even the manufacture of dry colors, such as chrome yellow, Prussian blue, chrome green, etc., which are purely chemical colors—and the reaction can be figured out molecularly—was carried on by men who had what they thought were secret formulas, and if more of one liquid than another was added, no note was taken of it. The mixed paint industry was also in a somewhat chaotic state, but a few men came to the realization that white lead was not the only pigment, and linseed oil and turpentine not the only vehicles which could be used. The mixed paint consumption to-day amounts to eighty million gallons per year, and such materials as barytes, blanc fixe, lithophone, sublimed white lead, silica, etc., are now regarded as beneficial accessories, rather than adulterants.

With the co-operation of the Department of Agriculture, such vehicles as soya bean and china wood oils are receiving marked attention. China wood oil is to-day such a necessity that the revolution in China, which has brought the price of the oil up to

$1.10 per gallon, has made it apparent that the paint and varnish manufacturer must have it at any price.

The shortage in the crop of flaxseed has not produced that tremendous market disturbance which was feared two years ago, for many prominent chemists have published methods for the use of Menhaden fish oil, which in many respects has shown itself to be at least as good as linseed oil.

The same condition has prevailed in the turpentine market, for in March, 1911, when the price reached $1.13 per gallon, the United States Navy decided that for its work a good turpentine substitute made from petroleum would answer its requirements, and the government is now using thousands of gallons of turpentine substitute for which it pays from twelve to fifteen cents per gallon. As the Navy purchased in 1910 about $70,000.00 worth of turpentine, this innovation has had a tremendous effect on the turpentine market, and the chances are it will never see such an abnormally high price again.

There seems to be a difference of opinion, all over the United States, regarding the materials to be used for paint, for it is conceded that paint should be made for the purpose for which it is intended, and should not necessarily be made of the highest priced materials which will produce that result. The Battleship Gray which the Government has partially adopted for the navy is made of 45 per cent. zinc oxide and 45 per cent. barium sulphate, with the necessary tinting material to produce the shade. A paint made of such materials costs about 25 per cent. less than the lead and zinc paints which were formerly used. The results showed that the zinc oxide and barium sulphate paint dried with a harder film and was not affected by salt water as much as the lead paint formerly used.

A similar condition of affairs has developed in the maintenance departments of the large railroads of the United States, and they have come to realize that no single pigment is as good as a mixture of pigments, and no single pigment is as good as a pigment which contains a reinforcing material in limited amounts.

The trend of opinion among paint manufacturers seems to be that they are more inclined to talk freely than they have been heretofore. Twenty-five years ago a paint manufacturer regarded a formula which he had as a valuable secret, but chemists who have made a specialty of the analyses of paints and their syntheses have shown that the average pigment mixed with oil, dryer and a volatile thinner is not a difficult mixture to analyze, and many of the secrets of the ignorant paint manufacturers have been exposed for their own benefit. Instead of having what they thought were valuable secrets, they had in many instances only mediocre formulas, which they improved when they saw what their competitors were doing.

Paint is so largely an engineering material that a knowledge of its composition is not to be treated lightly, and must not be regarded as an extravagance. Paint for decorative purposes presents new problems. The question of hygiene has entered so much into the use of paint that the wall paper manufacturers in England are now going into the manufacture of interior wall paints because people want washable walls in preference to those which harbor filth and germs.

MAXIMILIAN TOCH.

ORIGINAL PAPERS

CARBON BRUSHES.

By W. R. WHITNEY.

Received January 24, 1912.

The object of this paper is to describe some experiments which are being carried out with the view of assisting in an improvement in the qualities of motor and generator brushes, particularly of the carbon type. It is well known that while there have been very many improvements in all sorts of electrical apparatus during the past twenty years, there has not been a corresponding improvement in the quality of brushes, at least in this country. It is a peculiar commercial or manufacturing condition which all engineers will recognize when their attention is called to it—that an electrical manufacturing company usually puts upon its motors and generators all the legitimate accessories of its own make which are possible, excepting the brushes, and forces the users to purchase brushes from companies not necessarily in very close touch with electrical requirements.

If the brush was as simple an article of manufacture as the lag screw with which the apparatus is attached to the floor, this would not be serious, but quite a different condition exists. In fact, I think it is safe to say that a poor carbon brush, or brush of a wrong type, may render inoperative any kind of electrical apparatus. When one considers the stoppage of a long line of electric cars or the temporary shut-down of a generating plant, because of defects in a brush, one wonders that the demands have not already made an art of brush-making. One finds, in fact, that the production of this very essential, unobtrusive little block of carbon has had hardly any study at all.

Every electrical machine is carefully designed in detail as to size and shape of copper, iron and insulation, all of which vary with each machine, but as yet the important characteristics of a brush are not included in the design, although some one grade of brush is expected to operate satisfactorily over a great range of design. As long as this unfortunate condition exists, the best that can be hoped for is a brush which will do fairly well for a large number of machines, very well on a few and cause continuous trouble on a small balance until investigation of the constants of the particular machine, or its operating condition, shows the need of a different type of brush.

The careful investigation now in progress leads us to hope that the various characteristics of carbon brushes will soon be sufficiently understood, so that before long the designers of dynamos and motors will be enabled to use a brush exactly fitted to a particular design of machine, rather than a brush which does fairly well on machines of that general size and character.

Apparently the carbon brush was first made from such stock as is used for arc lamp electrodes and dry cell carbons. It was mixed, molded and baked in practically the same way, and the prices fixed on that basis. We have experimented with the understanding that a product might be producible which could bear a ten-fold greater cost of production than ordinary carbon brushes, and it is probable that our present methods are not far from this condition.

In what we call the early days, the motor or generator brush consisted of a brush of leaves of copper, and this had to be treated with the best of care. It was frequently cleaned and oiled and on some types of machines gave much trouble. It was usually set at an angle, so that the ends of the laminae bore upon the commutator. Any reversal of direction of rotation, as has frequently to take place in such apparatus as railway motors, was out of the question with this kind of brush. A block of solid copper bearing directly upon the commutator on such machines causes arcing and spattering of the metal, as there is a relatively high current passing from one commutator segment to the adjacent segment, through that part of the brush which connects them. This was a reason for laminae in the brush.

Our first experiments were taken up along the line of previous methods of manufacture and attempts were made to get at some sort of life tests and standards of comparison. We tried to learn what a good brush had to do and how long it might be expected to do it. In lamp manufacture the testing is an art by itself. An incandescent lamp is made to burn a certain time at a prefixed efficiency. We questioned whether a carbon motor brush could be submitted to similar life and quality tests. We recognized the importance of learning, if possible, what physical properties or constants for brushes would help in determining quality for electrical uses. The art is undeveloped, so that there is no considerable agreement between engineers even on important points. For example, it would be made clear by one engineer that a brush must be much softer than copper, so as not to wear away the commutator, and must not contain any hard spots because these might take up metal from the commutator. Against this was the equally powerful argument that the brush must be harder, so as to cut mica, and prevent the insulation finally protruding above the copper, and for this reason, carborundum, the hardest practical material, has been experimentally introduced into brush material. That the contact resistance should be relatively high and the body resistance low, were also practical suggestions. In order to operate systematically, we attempted to choose properties or tests to which numerical values could be attached. It was not assumed that all or even any of these factors could be interpreted strictly in terms of brush quality, but some such system of coordinating and comparing experimental products seemed necessary. We would naturally welcome suggestions leading to better tests. There were finally adopted measurements of hardness, tensile strength, density, electrical resistivity and such mechanical tests as chip and fracture tests.

The hardness is determined by the Shore Sclerescope, which consists essentially of a diamond-pointed weight which falls freely in a perpendicular glass tube and, striking upon the brush, rebounds to a height in the tube, which height is read from a scale. In general, the harder the material, the higher will be this rebound. In the case of brushes it distinguishes qualities over a range of about seventy units and is of considerable value in determining regularity of product.

A brush as made for railway motors and containing coke, graphite, lampblack, and binder carbon, if properly baked and fired, would have a hardness about 50, while if the firing be interrupted at say 500° C., its hardness value would be about 20. If the coke and lampblack be omitted, while the binder carbon is 3 per cent., and natural graphite be used, the hardness value will fall to about 16, even after firing for maximum hardness. In other words, such brushes as find common use on electrical apparatus may vary in hardness, depending upon the desired use, from 15 to 75 units of hardness.

The tensile strength is determined by cutting from the brush, held between steel guide plates, a definite testing piece of the carbon which can be held in the grip of the strength-testing machine and which will break at a point where the cross-section is exactly one-quarter square inch. The break is produced by the addition of shot at a definite rate to a pan supported by the test sample. The strength is expressed in pounds per square inch section.

The density compared to water is calculated from the weight of the brush and its physical dimensions.

The resistivity is determined by measuring the voltage drop across contact points $1^1/_2$ inches apart, which points bear heavily upon the brush when a current is sent through the brush. Separate contacts are used for the current. The accuracy of the measurement is about 3 per cent. of itself.

Some sort of chipping test seemed desirable because brushes in use often deteriorate and wear away, due to flaking off of chips from the edges of the bearing surface. This would be expected from the nature of the impacts given a brush when it chatters on a rough armature, revolving at high peripheral speed. The chip test we have used consists in a clamp for holding the brush firmly on a solid base or anvil, and in a weight guided by perpendicular rods, which weight falls from a fixed height and strikes the bearing face of the brush repeatedly at the same point, about a millimeter from the edge. The number of impacts necessary to force off a chip is called the chip test. This is quite surprisingly uniform for uniformly made brushes. It is usually weighted so that a brush of best quality will regularly chip after about 10 impacts of the weight when dropping from an increasing height in steps of 1 centimeter each.

Additional qualitative tests have resulted from comparison of product under different conditions. For example, the fracture or appearance of the fresh surface produced by breaking the brush across its longer dimensions discloses very effectively any irregularities produced by improper baking or pressing. This cross-section should be quite homogeneous and the fracture regularly conchoidal or square. No shelves, cracks or angular markings will be disclosed on breaking a well made brush. It is believed that such internal irregularities represent weakened structure, that even miniature cracks might take up and carry copper from the commutator and that breaking of a brush in use may often be attributed to internal cracks produced in the manufacture. Undoubtedly a rough commutator or heavy pressure of the spring of the brush-holder accounts for the breakage of many brushes in use, but in our tests on operating machines these variables are kept under control as much as possible.

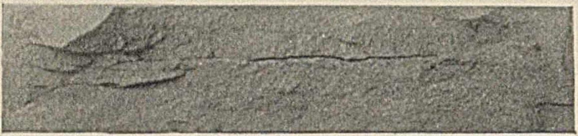

Fig. 1.

Fig. 2.

To illustrate this point, Figs. 1 and 2 are introduced. No. 1 shows a typical case of an improperly baked brush. The ingredients are the same as in 2, which was pressed and baked with greater care. The imperfections noted in 1 are produced by too rapid heating. They are not discoverable in the brush before breaking it. Neither of these is a squirted brush (*i. e.*, cut from a bar squirted through a die), both having been pressed to the desired shape from the powdered mixture.

The composition of the mixture from which the brush is molded has been varied greatly to suit various requirements, but, in general, it is made up of two or more of the four elements: lampblack, finely ground petroleum coke, graphite and some kind of tar or petroleum pitch which serves as a binder.

The effect produced by each of these ingredients is a different one; a suitable balance seems necessary and varies with the use of the brush. A brush made mostly of lampblack alone, with suitable binder, would be dense and hard, but of poor conductivity, and would cut copper badly. One made mostly of graphite is usually too soft and on ungrooved commutators, wears away too rapidly. The mica between the bars gradually protrudes and cuts the brush. Its electrical resistance is very low. One made mostly of coke is hard and of high resistance. It usually cuts the copper badly. The petroleum coke is used because of its uniformity and freedom from mineral matter. It can readily be appreciated that for some special purposes it may be well to incorporate hard polishing material into a brush, as where much mica has to be cut and where high conductivity and, therefore, much graphite is desired. The accidental grains of sand or such mineral impurities as often occur in ordinary coke, on the other hand, are to be carefully excluded.

It might seem that by using the above four forms of carbon (for the pitch leaves a fourth form of carbon, after the heat treatment), a satisfactory product could be obtained, and it has become apparent that the qualities may be varied over a wide range by proper variation of material; but the requirements are continually advancing, so that all sorts of experiments in composition, such as adding sulphur, special oils, etc., have been carried out.

It may be stated as a general rule that except for special conditions, the finer the state of subdivision of the brush ingredients, the better the quality of the finished brush. We have found, after having used ball mills, that the Raymond impact grinder pulverizes coke and similar materials very perfectly. We have found it desirable to grind not only the coke, but also the mixture of all the ingredients, to insure thorough mixing and a dense brush.

The finely divided materials, coke, lampblack and graphite, are placed in a mechanical dough mixer and a solution of the pitch in benzole is added and the whole kneaded for several hours. The benzole is then driven off by heat and the dried product, which is quite hard, is reground to about 200-mesh; this powder is compressed into brush form, in steel molds.

It was first thought that the best way to form the brush was to squirt bars of the mixture by means of an hydraulic press. These bars could then be cut to desired length. So far as our work went along this line, the product was not as satisfactory as when the brushes were individually pressed. Experiments were made in which various proportions of pitch binder were used. The temperatures of the press, mold and brush material were carefully controlled; special presses were built, etc., but irregularities often appeared in the product. The tendency of the material to flow unequally within itself during the passage through the die seemed to be responsible for cleavage planes and internal curved surfaces, which would often not develop until the brush was completed by baking and even then could be disclosed only by breaking the brush. We do not mean to conclude that a satisfactory brush cannot be made by squirting the hot mixture through a die, as the reverse is probably true, but for our purposes we finally adopted the accurate weighing of the mixture for each individual brush and the compression of this weighed material to an exact size in a mold under such a high pressure that additional pressure produces no further change. This pressure, for a standard railway motor brush, is about 25,000 lbs. per square inch. Above this pressure the quality is not appreciably affected; much below it, inferior product results as shown by density, resistance and strength. Marked effect is produced by variation in the temperature at which the mixture is pressed. For this reason care is taken to have the pressing done at about 25° C.

The pressed brushes are then packed in cast iron boxes, in lots of 100–200, and covered with a liberal layer of fine coke. A cast iron cover which fits the box well is then inserted and this, in turn, is covered with coke dust. A pile of these boxes is shown in Fig. 3. This box fits snugly into the electrically heated muffle shown in Fig. 4.

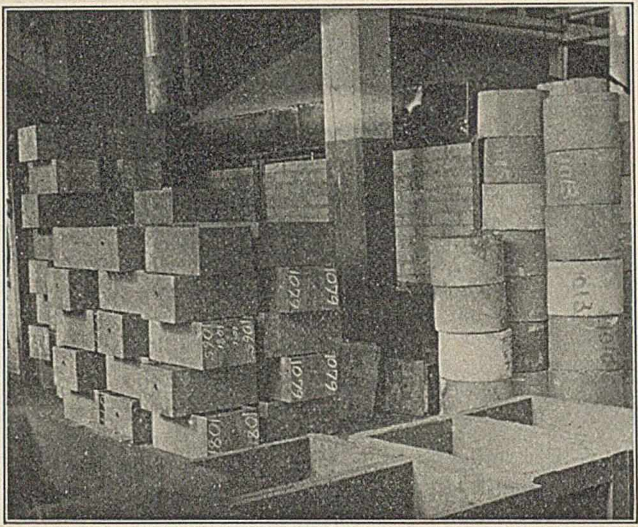

FIG. 3.

FIG. 4.

Early in the investigation it became evident that a large part of the irregularity of product, the shrinkage-cracks, etc., were to be attributed to a too rapid rate of rise of temperature during the early stages of heating the pressed brush. The pitch, or binder, which on its fractional distillation leaves the cementing carbon, which in turn largely determines the hardness and strength of the brush, is a mixture of organic compounds which liquefies at moderate temperature (100° C.) and rapidly evolves gases far below red heat. This led us to test methods of electric heat, and the rate of distillation of the volatile materials at gradually rising temperature was determined. This work resulted finally in the adoption of a very small type of muffle, for commercial production, which had a capacity for not over 200 brushes. It was heated by a special resistance wire and the temperature controlled by a thermo-element and resistance, so that the rate of rise of the temperature on each lot of brushes was about 5° C. per hour over a period of about 100 hours. The distillation of the binder under this treatment does not rupture or weaken the brush.

When large volumes of brushes are heated or the heating of small containers in a large furnace of usual type is carried out, the brushes near the walls receive a very different heat treatment from those near the center of the furnace. This causes much irregularity of product so that we still give all brushes the first firing or baking in the small wire-wound and heat-insulated muffles, of which No. 4 is an illustration.

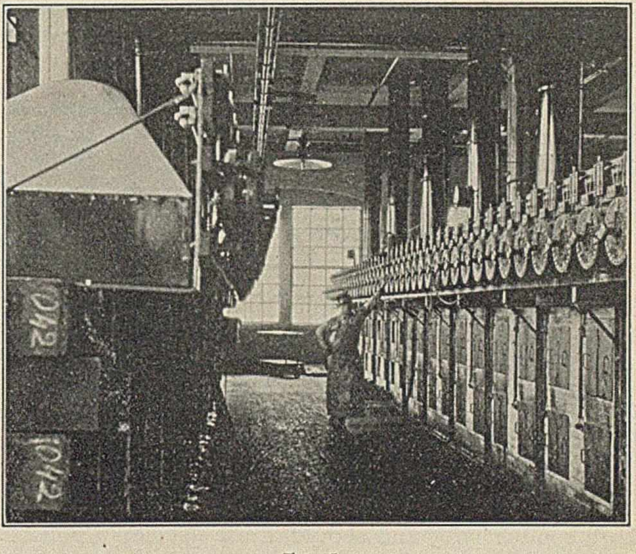

FIG. 5.

Fig. 5 shows a double row of these muffles with their control resistances. These latter enable the operator to gradually raise the temperature in each muffle. The rate of this rise is learned by means of pyrometer couples inserted into the muffle. In this, which is a preliminary heating only, the temperature rises during 100 hours to 500° C. In this process the volatile products of distillation have been so slowly eliminated from the brush that no striae, laminations, splits or blisters are produced. The brush is now bound together by a material largely carbon, but still capable of further shrinkage, hardening and decomposition by higher temperature.

After the preliminary heat at 500° C. the brushes are unpacked and a series of tests show relatively inferior qualities throughout, about as follows, for one type of railway motor brushes:

Hardness.	Tensile strength.	Resistance.
20	900 lbs. per sq. in.	0.043 ohm per inch cube

The material can still shrink greatly and improve by a higher heat treatment. This is accomplished in an ordinary porcelain kiln at about 1400° C., the brushes being packed as before, though not in iron, but in fire clay containers or saggers, the whole being covered with coke dust and the cover carefully luted on. The slightest carelessness in this protection process causes a softening of the outer surface of the brush, where a little combustion has removed the binder-carbon. This binder-carbon is still combustible in the presence of an excess of coke powder.

Owing to the severe requirements for railway motor brushes, the work for a long time was devoted exclusively to this field and there is probably still plenty of improvement possible.

As the work has advanced, the refinements of requirements have become more and more apparent, and it is quite evident now that several different carbon brush types are necessary to satisfy the requirements for different types of machines. In case of this particular brush, however, it is worth attention that by slight modifications in the process, such as fineness of grinding, pressure on the hydraulic press, etc., the record of tests kept during the past 2 years shows the following changes:

	Hardness.	Resistance.	Tensile strength.
1909	52.3	0.00135	1800
1911	58–60	0.00120	2700

Attempts were made to operate without change in the components, as weighed out; all qualities have improved through small refinements.

Development of the railway brush led to trying the same product on other types of electrical apparatus, and it was at once evident that the general brush requirements call for more than one kind of brush and more than a single composition. Generator brushes, while they do not meet the severe conditions met by railway motor brushes and may therefore be softer and of lower physical tests, should have high conductivity and should in use develop a polished commutator without cutting or smutting the metal. A fairly satisfactory type of generator brush may be made almost entirely of ash-free graphite and binder-carbon and will have approximately the following values on test: Hardness, 35; resistance, 0.00078; tensile strength, 2500; chip test, 6. It has been found that a brush needs some lubrication qualities which are difficult to express quantitatively. In the past it has even been customary to treat some brushes with oils, vaseline, etc., to give them this lubricating effect. It has also been found possible to improve operation of a commutator by using hard, strong, non-lubricating brushes and to interpose in several of the brush-holders a pure graphite brush, which serves to give desired lubrication for the other brushes. This has led to experiments on a combination brush, of which a section is shown (Fig. 6). In this case, by a proper selection of proportions of binder or pitch and the mixture, it has become possible to gain the same shrinkage in the two widely different materials, a hard brush body and a body largely composed of graphite. A sort of laminated brush is thereby produced and if there were service demands for such laminated brushes they could be produced.

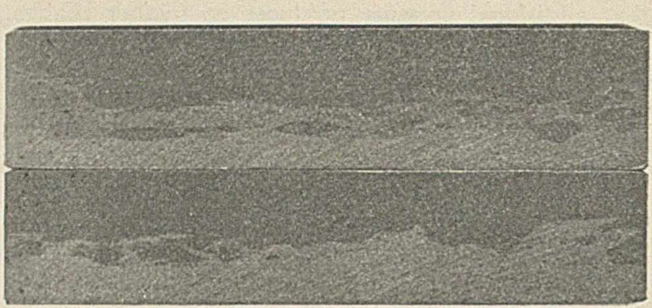

FIG. 6.

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THE RELATION OF THE REFRACTIVE INDEX OF SODA LIME GLASSES TO THEIR CHEMICAL COMPOSITION.

By EDWIN WARD TILLOTSON, JR.

Through the researches[1] of Abbe, Schott, Winkelmann and others, it has been shown that many of the physical constants of glasses may be roughly calculated, with the aid of empirical factors, from their chemical composition. In all of those calculations it was assumed that the constant of the glass was the additive sum of the empirically determined constants of the oxides present, and it was shown that these empirical constants, since they must contain an element characteristic of the manner in which the oxide is combined in the glass, may be very different from the constant of the corresponding pure oxide. No data was presented for calculating the refractive index, although, both from the scientific and industrial standpoints, it is one of the most valuable of constants.

Many expressions for the relation of the refractive index to the density of a substance have been developed, but only two have theoretical significance. The first of these, $\frac{N-1}{d} = K$, was proposed[2] by Gladstone and Dale and the second, $\frac{N^2-1}{N^2+2} \times \frac{1}{d} = K$, was simultaneously and independently developed by Lorenz[3] and Lorentz.[4] In both of these expressions K, the specific refractive power, is a constant which is supposedly independent of the temperature, and which is defined by the chemical composition and constitution of the substance. Many exceptions to this rule occur, however, and the expression of Gladstone and Dale fails completely when the vari-

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[1] "Jena Glass and its Scientific and Industrial Application," Hovestadt.

[2] *Phil. Trans.*, **337**, 1863.

[3] *Wied. Ann.*, **11**, 70 (1880).

[4] *Ibid.*, **9**, 641 (1880).

ation of temperature is sufficient to produce a change of state in the substance. Both expressions hold fairly well, however, for liquids and solutions. In a solution or a homogeneous mixture of liquids, which do not react to form a compound, the specific refractive power is an additive function of the respective refractivities of the compounds present and may therefore be calculated as follows:

$$K = \frac{p_1K_1}{100} + \frac{p_2K_2}{100} + \frac{p_3K_3}{100} + \ldots\ldots$$

in which p_1, p_2, p_3, etc., are the percentages in which the several compounds are present, and K_1, K_2, K_3, etc., are their respective specific refractivities.

Very few attempts have been made to apply this relation to glasses or to pure silicates. Larsen[1] has shown by some very accurate measurements on carefully prepared silicates that the specific refractive power is additive within limits of error in case of mixtures of calcium and magnesium metasilicates, and of albite and anorthite. both in the vitreous and the crystalline form. A marked difference, however, occurs in the values of the specific, refractive power for the vitreous and crystalline compounds of like composition.

This paper is an account of an investigation on the refractive index and the specific refractive power of some soda lime glasses for the purpose of obtaining data, whereby these refractive indices might be calculated from their composition with a fair degree of accuracy. The glasses were prepared from pure sodium carbonate, pure calcium carbonate and a high grade of glass sand which analyzed 98.5% SiO_2, the remainder being chiefly aluminum oxide and moisture. The ingredients were carefully weighed out, well mixed and finally fused in clay crucibles in an oxidizing atmosphere of a gas furnace. When the glass was "plain" it was poured out on cold iron plates and, after annealing, was broken into small fragments. The refractive index for white light was measured with the aid of an Abbé refractometer using selected fragments of the glass which presented a smooth, flat surface of the original plate. With a little care in selecting plane fragments of the glass, the values of the refractive index for successive plates usually agreed to within two or three units in the third decimal place, and the average of a number of readings was finally taken.

It is evident that, in the procedure as set forth, there are several chances for error. The glass could not be obtained free from striae in one or even two fusions when clay crucibles were employed, owing to the solvent action of the glass on the crucible; and the melts were stirred very little, therefore, in order that as few impurities as possible should be introduced. It is improbable that the lack of homogeneity, as shown by striae, introduced a very marked error, since the refractive indices of successive preparations[2] of the same glass, measured on carefully ground and polished plates, agreed to within two units in the third decimal place. That this is within the limit of error for glass prepared in clay crucibles is shown by the fact that, even in the manufacture of optical glass, which must possess homogeneity to the highest degree, it is customary[1] to find a difference in a large plate amounting to several units in the fourth decimal place and not uncommon to find a difference of one unit in the third decimal place, and also by the fact that manufacturers cannot vouch[2] for the refractive index of a crown glass to within two units, or for a flint glass to within six or eight units in the third decimal place. The errors arising from preparation and from optical measurements are therefore probably small in comparison to those introduced into the values of the specific refractivities by the use of the calculated densities. It has been shown in a previous paper[3] that the densities of many glasses may be calculated with a moderate degree of accuracy, from the chemical composition. The average error in these computed densities was about one per cent., but occasionally amounted to two per cent. An error of one per cent. in the density produces an error in the refractive index, when it is about 1.5, of five units in the third decimal place, and about one unit in the second place when it is 1.6. In the specific refractivity (Lorenz and Lorentz), one per cent. error in the density introduces an error of from 0.0005–0.0010. It is also possible that an additional error was introduced in the composition of the glasses. No analyses of the glasses were made, but the composition was assumed to correspond to that of the "batch." This error is doubtless small in comparison with other errors since Kultascheff[4] has shown that, although the loss on heating pure sodium metasilicate may amount to 4%, as the percentage of calcium silicate increases the loss rapidly decreases and becomes negligible; and Day and Allen[5] apparently did not observe any noticeable volatilization in the synthesis of feldspar.

The results which were obtained are given in Table I. The first four columns of this table show the composition of the glasses, which correspond to mixtures ranging from $Na_2O.3SiO_2$ to $CaO.SiO_2$. In the fifth column are given the densities as calculated[6] from the composition; in the sixth, the observed refractive index for white light; and in the seventh, the values of K which were calculated from Gladstone and Dale's formula.

When these values for K are plotted in a system, in which the ordinates represent the composition and the abscissas the specific refractivities, as shown in Fig. 1, it becomes evident that they form two straight lines which intersect at a point corresponding to a glass of the composition $2Na_2O.3CaO.9SiO_2$. This break in the curve, therefore, indicates the existence of a compound at this point. It is especially significant since both Kultascheff[7] and Wallace[8] have

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

[2] Unpublished data.

[1] Zscholke, *Zeit. für Instrumentenk*, **29**, 286.

[2] Hovestadt, *loc. cit.*, p. 18.

[3] Tillotson, THIS JOURNAL, **3**, 897 (1911).

[4] *Z. anorg. chem.*, **35**, 187 (1903).

[5] "The Isomorphism and Thermal Properties of the Feldspars."

[6] Hovestadt, *loc. cit.* Tillotson, *loc. cit.*

[7] *Z. anorg. Chem.*, **35**, 187 (1903).

[8] *Ibid.*, **63**, 1 (1909).

Table I.

$CaSiO_3$ mol. Per cent.	SiO_2. Per cent.	CaO. Per cent.	Na_2O. Per cent.	D calc.	N obs.	K obs.	K calc.	N calc.	N calc.-obs.
00	74.45	0.00	25.55	2.37	1.5000	0.2110	0.2110	1.5000	0.0000
10	73.60	2.50	23.90	2.395	1.5060	0.21127	0.2111	1.5055	—0.0005
20	72.32	5.18	22.50	2.42	1.5115	0.21137	0.21118	1.5111	—0.0004
30	70.85	8.25	20.90	2.45	1.5172	0.21110	0.21125	1.5175	+0.0003
40	69.30	11.70	19.00	2.48	1.5240	0.21129	0.21135	1.52410	+0.0001
50	67.40	15.60	17.00	2.52	1.5334	0.21166	0.2115	1.5330	—0.0004
50	67.40	15.60	17.00	2.52	1.5300	0.21032	0.2115	1.5330	+0.0030
60	65.20	20.20	14.60	2.57	1.5432	0.21137	0.2116	1.5438	+0.0006
70	62.75	25.35	11.90	2.63	1.5590	0.21254	0.2127	1.5594	+0.0004
80	59.60	31.80	8.60	2.705	1.5800	0.21442	0.2142	1.5794	—0.0006
80	59.60	31.80	8.60	2.705	1.5796	0.21436	0.2142	1.5794	—0.0002
100	51.85	48.15	...	2.92	1.628[1]	0.21517	0.2178	1.6307	+0.0027

[1] —N_{na}—Larsen, *loc cit.*

observed that in mixtures of sodium and calcium metasilicates a maximum melting point is reached at the composition $2Na_2O.3CaO.5SiO_2$. In column 8 (Table I) are given the specific refractivities, as indicated by the two straight lines in Fig. I; column 9, the refractive index computed from columns 5 and 8; and column 10, the difference between the calculated and observed values of the refractive index.

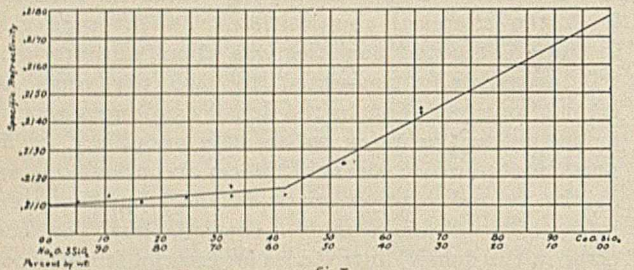

Fig. I

In Table II are shown similar data for these same glasses, calculated from the formula of Lorentz and Lorenz, and in Fig. 2 the graphic relation of the specific refractivities to the composition. It will be noticed that the same break is observed in the refractive curve as shown by the full lines in Fig. II.

Table II.

$CaSiO_3$ mol. Per cent.	D calc.	N obs.	K′ obs.	K′ calc.	N calc.	N calc.-obs.
00	2.37	1.500	0.1241	0.12422	1.5006	+0.0006
10	2.395	1.506	0.12406	0.12389	1.5054	—0.0006
20	2.42	1.5115	0.1239	0.12349	1.5110	—0.0005
30	2.45	1.5172	0.12351	0.12361	1.5176	+0.0004
40	2.48	1.524	0.12338	0.12346	1.5244	+0.0004
50	2.52	1.5334	0.12329	0.12323	1.5333	—0.0001
50	2.52	1.530	0.12260	0.12323	1.5333	+0.0033
60	2.57	1.5432	0.12272	0.12300	1.5450	+0.0018
70	2.63	1.559	0.12277	0.12270	1.5586	—0.0004
80	2.705	1.580	0.12305	0.12236	1.5761	—0.0039
80	2.705	1.5796	0.12298	0.12236	1.5761	—0.0035
100	2.92	1.628[1]	0.12155	0.12150	1.6276	—0.0004
	2.43[2]	1.5096	0.12300	0.12291	1.5093	—0.0003

This break is, however, less marked than in the case shown in Fig. I, and all of the specific refractivities may, for convenience, be considered to lie upon a single straight line indicated by the dotted line in the figure. This behavior of the N^2 formula, that of minimizing the effects of compounds on the specific refractivity, makes it possible to calculate the specific refractivities directly from the percentage composition of the glass. Since the specific refractivity is, within the limits of error, linear, it may be computed by means of the following equation:

$$K = \frac{P_1K_1}{100} + \frac{P_2K_2}{100} + \frac{P_3K_3}{100}, \text{ etc.}$$

in which P_1, P_2, P_3, etc., are the percentages of the oxides, and K_1, K_2, K_3, etc., are the empirically determined specific refractivities of the oxides. For soda lime glasses these are as follows:

SiO_2	0.1220
CaO	0.1210
Na_2O	0.1302

Columns 5 and 6 of Table II show the specific refractivities and refractive indices as calculated by the aid of these factors and column 7 the difference between the calculated and observed values of the refractive index. Not only are the computed values for the glasses given above sufficiently accurate for many kinds of work, but the last glass in Table II shows that the refractive index of glasses richer in silica, may also be calculated with equal accuracy.

Although, in employing this method for estimating the refractive index, no consideration is taken of the compounds which may be formed, yet it is theoretically correct up to the point where the compound is found, and is applicable to the majority of soda lime glasses; for these rarely contain as large a proportion of lime as the ratio $2Na_2O.3CaO.xSIO_2$ calls for, and they therefore lie to the left (Figs. I and II) of the break in the specific refractivity curve, and in the region for which the factors, given above, furnish the most satisfactory agreement. It must be remembered, however, that the factors employed represent not the true specific refractivity of the pure oxide, but the true refractivity modified by the nature of the silicate which is formed and also by the inexact values of the density which is employed in the calculations. This is well illustrated in Table III, in which are shown the refractive indices of several oxides, together with the density observed, the density em-

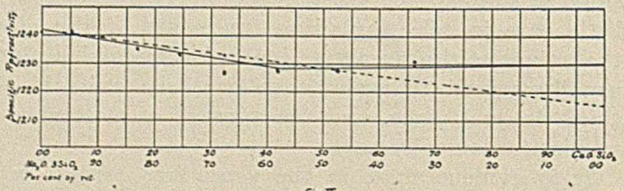

Fig. II

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[1] N_{na} Larsen, *loc cit.*

[2] SiO_2, 77.7%; CaO, 8.5%; Na_2O, 13.8%.

ployed in the computations and the specific refractivities calculated from them, together with the factors given above.

TABLE III.

		N.	D obs.	D calc.	K obs.	K calc.[2]	K[3].
SiO_2	Quartz......	1.5472[1]	2.652[1]	2.3	0.11961[1]	0.1380	0.1220
	Trydymite..	1.4830[1]	2.318[1]		0.12319[1]	0.1240	
	Fused Quartz	1.4590[1]	2.213[1]		0.12354[1]	0.1188	
CaO..............		1.8320[1]	3.316[1]	4.1	0.13266[1]	0.1073	0.1210

SUMMARY.

1. A series of soda lime glasses have been made and their refractive indices measured.

2. The existence of a double silicate of the type $2Na_2O.3CaO.xSiO_2$, which is doubtless the double metasilicate, described by Kultascheff and Wallace, has been made evident.

3. The specific refractivities of these glasses, computed with the aid of the calculated densities, are additive from pure sodium silicate up to the composition in which the molecular proportion of soda to lime is 2 : 3.

4. Factors have been derived by means of which the specific refractivity of soda lime glasses may be calculated. These are for the formula of Lorentz and Lorenz: SiO_2, 1220; CaO, 1210; Na_2O, 0.1302.

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A NEW METHOD FOR THE DETERMINATION OF VANADIUM.

By D. J. DEMOREST.

Received September 25, 1911.

The following method for the determination of vanadium in steel depends upon the selective oxidation of ferrous sulfate in the presence of vanadyl sulfate by means of manganese dioxide. The vanadyl sulfate is then titrated by adding an excess of permanganate, the excess permanganate being titrated by sodium arsenite.

This differential oxidizing action apparently contradicts the results of J. R. Cain,[4] who found that both iron and vanadium are oxidized, but the reasons for this discrepancy are shown in the note which follows on page 256.

The manganese dioxide should be sufficiently fine to pass through a 200-mesh sieve, and yet should settle in a beaker of water in 30 seconds.

The process in detail is as follows: In a 500 cc. flask a two-gram sample of the steel or iron is dissolved in a mixture of 30 cc. of water and 12 cc. concentrated H_2SO_4 with application of heat. Then one cc. of HNO_3 (sp. gr. 1.42) is added cautiously to oxidize the iron and the solution is boiled for a few minutes to remove the nitrous fumes. Then the solution is diluted with 30 cc. of water and a strong solution of $KMnO_4$ is added to completely oxidize all carbon, etc., and the solution is boiled. If the permanganate or the resulting MnO_2 should disappear, not enough permanganate has been used, and more should be added. Now ferrous sulfate is added to reduce the MnO_2, $HMnO_4$, H_2CrO_4, and H_3VO_4, etc., and the solution is again boiled to remove any possible nitrous fumes. Then pure distilled water is added to make the volume about 250 cc., $N/10$ $KMnO_4$ added until the solution is pink, and the solution cooled to tap water temperature. Ferrous sulfate solution is added until all reducible compounds including chromic and vanadic acids are reduced. Only enough ferrous sulfate should be added to be certain that there is a decided excess present. A solution, one cc. of which equals about 0.01 gram of iron, is the one used. Now about one gram of C. P. MnO_2 is added and the solution shaken vigorously. After two minutes a drop is tested with ferricyanide on a white plate to see if the iron is completely oxidized. It generally takes from four to six minutes. At the end of each minute the solution is tested for ferrous iron until none is present and the shaking is continued for about one-half minute longer. It should be noted that a bluish color will always be obtained in the presence of vanadyl sulfate after the test drop has stood for a few seconds. The end should be taken when the test does not show blue immediately. The blue color which forms after a few seconds, even when there is no ferrous iron present, is due to the reduction of ferri- to ferrocyanide by the vanadyl sulfate. One can become familiar with this end by adding a drop of ferric sulfate containing vanadyl sulfate to a drop of ferricyanide on a white plate.

The MnO_2 oxidizes the ferrous sulfate to ferric sulfate, but does not oxidize the vanadyl sulfate $[V_2O_2(SO_4)_2]$. Then the MnO_2 is filtered off on an asbestos mat, using suction. From a burette a standard solution of $KMnO_4$ is added until a pink tinge is present in the solution, and one cc. more is added. and after one minute the excess permanganate is titrated with Na_3AsO_3 solution. The end point is very sharp. If at this point the operator is not satisfied with this titration, the excess arsenite may be oxidized with $KMnO_4$, ferrous sulfate again added, then oxidized with MnO_2 as before, and the titration repeated, thus giving a check on the titration. A blank determination must be run on a vanadium-free steel, and the result deducted. The blank generally amounts to about 0.00075 gram V. The time required is about one-half hour and the results are very satisfactory. In fact the accuracy is about that of a phosphorus determination.

The vanadium steel standard furnished by the Bureau of Standards was analyzed by the above method. The result of the Bureau chemists is 0.0143 per cent. V and the average of the coöperating chemists is 0.15 per cent. V. The writer obtains the following results, the average being 0.143 per cent.:

0.140	0.138
0.147	0.147
0.143	0.143

To further test the method, two-gram samples of

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[1] Larsen, *loc. cit.*

[2] Using Lorentz and Lorenz formula and "D calc."

[3] Factors used in computing specific refractivities.

[4] THIS JOURNAL, **3**, 476 (1911).

vanadium-free steel with the addition of ferro-vanadium containing 0.00684 gram of vanadium were analyzed. The results were 0.00680 and 0.00690 gram V. Another sample with 0.0342 gram V was analyzed, and 0.03432 gram V was found.

To test the effect of chromium on the method, the Bureau of Standards' sample above mentioned was analyzed with the addition of 0.100 gram Cr. The results were 0.143 per cent. and 0.143 per cent. V, showing that chromium has no effect on the vanadium results. Scores of other determinations have been made, proving the accuracy of the method.

The $KMnO_4$ solution used equals 0.001 gram iron per cc., and the arsenite solution has the same strength. This makes the $KMnO_4$ equal 0.000917 gram vanadiun per cc. The arsenite solution is made by dissolving about 2.25 grams As_2O_3 in Na_2CO_3 solution and diluting to 2,000 cc.

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A RAPID METHOD FOR THF DETERMINATION OF VANADIUM IN STEELS, ORES, ETC., BASED ON ITS QUANTITATIVE INCLUSION BY THE PHOSPHOMOLYBDATE PRECIPITATE.

By J. R. Cain and J. C. Hostetter.

Received December 27, 1911.

I. INTRODUCTION.

The fact that vanadium is carried down with ammonium phosphomolybdate when the latter is precipitated in solutions of the former has long been known. Likewise, the fact that the precipitate so obtained has different properties from the normal phosphomolybdate has been mentioned by several authors. The orange to brick-red color of this vanadium-bearing precipitate is quite different from the color of the normal ammonium phosphomolybdate, called from its color the "yellow precipitate." Brearley and Ibbotson[1] mention the increased solubility in dilute nitric acid of the vanadium-bearing precipitate over the normal precipitate, and give some conditions to lessen precipitation of vanadium with phosphorus in steel analysis. The phenomenon has usually been studied with regard to the determination of phosphorus in the presence of vanadium, since the precipitation of vanadium with ammonium phosphomolybdate interferes with an exact determination of phosphorus by the ordinary methods. Especially is this true in steel analysis. The possibility of easily separating vanadium from iron by this method has, we believe, never been studied before. The present research was undertaken in order to decide whether or not vanadium could be completely precipitated with phosphoric acid, and, if so, to learn if it could be determined quantitatively.

2. PRELIMINARY CONDITIONS FOR PRECIPITATING THE VANADIUM.

The necessary ratio of phosphoric acid to vanadic acid for complete precipitation of the latter was investigated qualitatively by following the change in color of the phosphomolybdate precipitated with increasing additions of phosphoric acid. A nitric acid solution of a vanadium-free steel was prepared; to this was added a known amount of vanadium from a carefully standardized ammonium vanadate solution. To equal volumes of the steel solution so prepared were added gradually increasing volumes of a roughly standardized sodium phosphate solution, and the phosphoric acid was precipitated by the molybdate reagent, observing the conditions for this precipitation usually given in texts on steel analysis. With small amounts of phosphoric acid the precipitate was of a deep orange color, which became progressively lighter as the phosphorus increased, finally approaching the color of the normal or vanadium-free phosphomolybdate when relatively very large amounts of phosphoric acid were added. The filtrates were treated by precipitating a further small amount of phosphoric acid, and judging by the color of the precipitate whether or not precipitation was complete the first time. The color of the precipitate proved to be a very delicate qualitative criterion, and very soon it was possible in this manner to fix with fair accuracy the ratio of phosphoric acid to vanadic acid in order to carry down all the vanadium with one precipitation. As methods for the quantitative determination of the vanadium were developed this ratio was determined with greater accuracy. The mechanism of the precipitation and the question of this ratio are subjects that will be described in more detail in another paper. It is sufficient for the present purpose to say there is a co-precipitation of vanadium under the above general conditions, which can be controlled accurately enough to make the precipitation uniformly quantitative. The conditions will be detailed later.

Other questions affecting the probable accuracy of the determination were (1) the solubility of the vanadium-bearing precipitate in the usual washing solutions, and (2) the optimum temperature for precipitation. As to the solubility of the precipitate, it was soon found that the presence of vanadium caused marked changes in the solubility of ammonium phosphomolybdate. It was noticed that when the precipitate dissolved to any extent in the washing solutions these were strongly colored, usually having a straw or orange tint. It was thus possible to decide this question qualitatively, and Table I gives some of the results obtained. It will be seen that acid ammonium sulfate and ammonium nitrate solutions are best adapted for washing the yellow precipitate. Incidentally, the marked solubility in dilute solutions of potassium nitrate and of nitric acid is of interest, for these are the wash solutions recommended by some authorities for use when determining phosphorus in steel. It is evident that such use may occasion errors in the phosphorus determination if vanadium is present in appreciable amount. It seems probable that the solubilities vary considerably with the proportion of vanadium present in the precipitates.

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[1] "The Analysis of Steel Works Materials," **1902**, p. 165.

TABLE I.—ORDER OF SOLUBILITY OF VANADIUM-BEARING PRECIPITATE[1] IN VARIOUS SOLVENTS AT ROOM TEMPERATURE.

Solvent.	Concentration.	Color of solution.
Ammonium acid sulfate[2]		Colorless
" nitrate	Saturated solution	"
" "	10 per cent.	"
" sulfate	50 "	Faint yellow
Nitric acid	50 "	Color increases regularly down the series, showing increasing solubility
"	25 "	
Ammonium sulfate	30 "	
" nitrate	1 "	
" chloride	1 "	
" sulfate	10 "	
Sulfuric acid	50 "	
Water	..	
Ammonium molybdate (neut.)	1 "	
Potassium nitrate	1 "	
" sulfate[3]	1 "	Deep yellow (complete solution).
Nitric acid[3]	1 "	
Sodium sulfate[3]	1 "	
Ammonium molybdate (neut.)[3]	10 "	

The optimum temperature for precipitation in this connection is governed largely by considerations affecting the physical properties of the precipitate and the speed of precipitation. Accordingly, our precipitations are made from solutions brought to boiling before addition of the precipitant, thus securing a rapidly settling precipitate readily filtered by suction. Certain theoretical reasons, to be considered at another time, likewise demand a precipitation at this high temperature. Brearley and Ibbotson[4] also have shown that more vanadium is precipitated at high than at low temperatures.

After having assured ourselves qualitatively that vanadium is completely precipitated by the phosphomolybdate precipitate obtained under proper conditions, a study was made of methods for determining the vanadium thus precipitated.

3. SEPARATING THE VANADIC ACID FROM THE MOLYBDIC ACID.

In view of the easy volatility of molybdic acid, it was at first thought practicable to heat the precipitate over a blast lamp until all the molybdenum had been driven off. It was found that nearly all the molybdenum could be volatilized, but there are too many difficulties encountered to make the method reliable. There is much danger of mechanical loss where the relative amount of vanadium is small; moreover, at the temperature required for rapid volatilization, the vanadium pentoxide remaining behind fuses and creeps over the side of the boat or crucible used as a container, a fact previously noted by Gibbs.[5] Further, there is usually a slight reduction of molybdenum to a lower oxide which does not volatilize readily. However, this method of handling the precipitate has some merits, particularly if one wants visual confirmation of the presence of vanadium in a sample of material. The characteristic appearance of fused vanadium pentoxide is easily distinguished in the residue after ignition, even though some of the lower (blue) oxide of molybdenum is present. Of course, this precipitate can be taken up by fusion with sodium carbonate and precipitated by mercurous nitrate or in any other manner desired. Usually it is accompanied by some iron oxide. We consider that the method is subject to too many irregularities and is too difficult of manipulation for technical work. Moreover, it is much slower than other procedures to be described later. We found that Truchot[1] had also proposed and made use of the volatility of molybdic acid to separate it from small amounts of vanadium coprecipitated with molybdenum, when electrolyzing ammoniacal solutions of molybdates and vanadates.

A very much simpler and shorter method has been devised by us for separating the vanadium in pure form from the phosphomolybdate precipitate. The latter is suspended in a small amount of hot water, and dilute ammonia added drop by drop, with vigorous shaking, until everything is in solution. The solution is heated until all but a trace of ammonia is expelled. The success of the operation depends on the presence of a very small amount of free ammonia at this stage. If too much ammonia is present, the precipitate subsequently obtained on adding mercurous solution carries down some molybdenum. On the other hand, enough ammonia must be present to form a sufficient volume of amido precipitate to bring down the vanadium. One or two trials will enable the operator to decide as to the proper excess. When the right amount of ammonia is present, the solution is filtered, if necessary, and enough mercurous nitrate solution is added to it to give an appreciable acid reaction with litmus paper.[2] Usually a voluminous black precipitate separates on shaking; if it does not form and settle rapidly, the solution is heated until it does. The precipitate is washed by decantation two or three times with water containing 1 per cent. mercurous nitrate, and is finally transferred to the filter and washed there two or three times more. Filter and contents are transferred to a porcelain crucible, the filter paper burned off, and the mercury volatilized. The vanadium remains partly as vanadic pentoxide, partly as lower oxides and is accompanied by relatively very little molybdenum. The latter may be precipitated, if desired, by hydrogen sulfide (after the vanadium has been dissolved out of the crucible with concentrated sulfuric acid and the solution diluted) leaving a pure vanadium solution. If the vanadium pentoxide is dissolved out of the crucible with concentrated sulfuric acid, the intense brown or orange color, characterizing such solutions of vanadium pentoxide is very characteristic; if blue or green tints (due to lower oxides of molybdenum and vanadium) are present, these disappear on the addition of a trace of nitric acid, and evaporation until dense strong fumes appear.

We have not used this method for obtaining quantitative separations of vanadium, although it would probably be successful if the filtrates were treated a second or third time, and the precipitates combined. However, by far the greater portion of the vanadium is obtained at first.

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[1] Containing approximately 0.4 per cent. vanadium.

[2] See p. 250.

[3] 0.5 gram of precipitate dissolves in less than 20 cc. of the solvent.

[4] *Loc. cit.*, p. 165.

[5] *Am. Chem. J.*, **5**, 371 (1883–1884).

[1] *Ann. chim. anal.*, **7**, 165–7 (1902).

[2] Caused by the hydrolysis of the mercurous nitrate solution.

The principal use we have made of these methods, as stated above, has been for the purpose of actually isolating the vanadium where there could be the slightest doubt as to its being present at all. In this manner, we believe, the value of the method, from a purely scientific standpoint, is increased. For technical or practical purposes it is never necessary to separate the vanadium from the molybdic and phosphoric acids in order to determine it accurately.

4. REDUCTION OF THE VANADIC ACID BY SULFUR DIOXIDE.

Edgar's method[1] of reduction by sulfur dioxide was next tried, with the idea of reducing the vanadium to the tetravalent stage without affecting the molybdenum; the tetravalent vanadium could then be titrated against permanganate, as usual. Edgar found that by properly adjusting the acidity (sulfuric acid) of his solution and its molybdenum concentration, the differential reduction could be made with ease. Our results are confirmatory, but unfortunately the method is limited in its application to the present problem because of the effect of the presence of iron occluded by the large amount of ammonium phosphomolybdate sometimes required. This iron is sometimes present in relatively large quantities and of course is wholly or in part reduced by the sulfur dioxide. It is difficult, too, to completely eliminate this impurity from the precipitate without unduly prolonging the process. Solution of the precipitate, followed by reprecipitation, helps but little. If the precipitate is dissolved in ammonia, a clear solution is obtained, even if considerable iron is present; the latter reveals its presence by imparting a dark color to the otherwise colorless solution. If, however, the precipitate is dissolved in sodium hydroxide, a large proportion of the iron separates and the precipitation can be made nearly complete by boiling the solution until all the ammonia of constitution of the yellow precipitate is expelled.

We made a number of fairly accurate determinations of vanadium in the presence of iron and chromium by precipitating the vanadium with phosphomolybdate, dissolving the precipitate in ammonia, acidifying with sulfuric acid to a 15 per cent. acidity, followed by sulfur dioxide reduction and permanganate titration. In most of the determinations it was necessary to get rid of the iron contaminating the phosphomolybdate by dissolving the latter in sodium hydroxide solution and filtering off the ferric hydroxide, as above. It was found that chromium in the trivalent condition did not affect the determination of vanadium at all.

A series of determinations by this method now gave the necessary data for accurately fixing the ratio of phosphorus to vanadium to secure complete precipitation. It was established that ten times as much phosphorus as there is vanadium to be determined would insure complete precipitation of all the vanadium and allow a sufficient margin of safety for variation from suspected composition. We have used this ratio in all subsequent determinations. Of course, where the vanadium content of a sample is not known within sufficiently close limits, it is necessary to make two or more phosphomolybdate precipitations, testing each for vanadium. However, this is about what one has to do with any method when working on unknown materials.

The method of reducing the vanadium by sulfur dioxide and titrating against permanganate having proved, in our opinion, too long and uncertain for technical use, other methods were tried.

5. COLORIMETRIC DETERMINATION OF THE VANADIC ACID.

Gregory's colorimetric method,[1] depending on the colors developed in strong sulfuric acid solutions of vanadium and strychnine, seemed promising, inasmuch as the phosphomolybdate is so soluble in concentrated sulfuric acid. We found by preliminary tests that the associated molybdenum has no appreciable effect on the strychnine, so far as color development is concerned. However, iron does, and this is to be expected from Allen's statement of the cause of the color:[2] "On treating a cold solution of strychnine in concentrated sulfuric acid with an oxidizing agent of almost any kind a rich purple-blue coloration is developed. This changes more or less rapidly through purple and crimson to a bright cherry-red tint, which is somewhat persistent." From this it was evident that ferric iron must be absent and probable that the vanadium must be in the pentavalent state. We confirmed the latter by trials of concentrated sulfuric acid solutions of V_2O_4, which gave no color with strychnine. This is an important point, for we found that strong sulfuric acid solutions of vanadium pentoxide are very prone to go over to the quadrivalent state, when of course they develop no color with strychnine. With sulfuric acid solutions of the phosphomolybdate precipitate containing vanadium it is easy to follow this change by the change of color in the solution. Initially there is a straw or orange color,[3] apparently due to the presence of acid vanadates or polyacids,[4] which is probably closely proportional to the amount of vanadium present, but after a few minutes' evaporation to strong sulfur trioxide fumes, and with low vanadium content, the solution becomes either colorless or a pale blue. We observed the same phenomenon with concentrated sulfuric acid solutions of vanadium pentoxide. At first the reduction was thought to be due to organic matter present in the sulfuric acid, but further experiments with larger amounts of vanadium showed too much reduction to be accounted for in this way. For instance, in one experiment 8 mg. of vanadium as pentoxide dissolved in 15–20 cc. of sulfuric acid were fumed in a carefully covered flask for four or five hours, at the end of which time

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[1] *Am. J. Sci.*, [4] **25**, 332 (1908). See also Gibbs: *Loc. cit.*

[1] *Chem. News*, **100**, 221.

[2] "Commercial Organic Analysis," Vol. III, 2nd Ed., Pt. II, p. 368.

[3] Some work has been done here toward making this color the basis of a colorimetric method for vanadium.

[4] Gmelin-Kraut, "Handb. d. Anorg. Ch.," 7th Auf., Vol. III, Pt. 2, p. 89.

reduction was practically complete. We found that Prandtl[1] had already investigated this matter and concluded that under these conditions there is a dissociation of the vanadium pentoxide in analogy to the behavior of chromic anhydride dissolved in concentrated sulfuric acid. This behavior was the opposite of what we had expected, after having read the work of Koppel and Behrendt,[2] who found the reverse action taking place. Possibly there is an equilibrium between the two sets of reactions. This complication is very troublesome when attempting to prepare the sulfuric acid solution of the vanadium-bearing phosphomolybdate for colorimetric estimation by strychnine. As stated above, with small amounts of vanadium (for which we had expected the colorimetric method to be very useful), the reduction or dissociation takes place completely in a few minutes after the precipitate is dissolved in sulfuric acid. Such a solution treated at once with strychnine either gives no color, or a much less intense color than corresponds to the actual amount of vanadium present. On the other hand, if the attempt is made to reoxidize the vanadium to the pentavalent stage, this must be accomplished under difficult conditions, for no excess of the oxidizer must be left in the solution (inasmuch as this would give a color with the strychnine), nor must the solution be heated unduly long in attempting, for instance, to destroy or drive off the excess of oxidizer, for as soon as the excess disappears the vanadium goes quickly to the quadrivalent stage. Thus, while it was easy to oxidize the vanadium with a minute quantity of nitric acid, we could never be sure that the excess had been driven off and at the same time no vanadium had been reduced. We attempted to find an oxidizing agent that would oxidize the vanadium without affecting the strychnine and found that bismuthate would do so under very special sets of conditions, but there were complications attending its use, such as clouding of solutions in the colorimeter, occasional unexplained development of color in blanks, etc., that led us to abandon its use altogether. Besides the uncertainties and complications occasioned by solution in concentrated sulfuric acid already mentioned, which necessitate oxidation with reagents liable to cause high results if used (or low ones if not used), and those arising from the presence of iron with the phosphomolybdate, necessitating reprecipitation, there is also the possible accidental introduction of organic matter at various stages where reduction of vanadium might occur, and the troublesome manipulation of concentrated sulfuric acid in the colorimeter. The colorimetric method of determining vanadium in the precipitate at first appealed to us because of its apparent simplicity and wide range of application, but the results of an extended series of determinations lead us, for the present, at least, to abandon these views.

6. REDUCTION OF THE VANADIUM BY HYDROGEN PEROXIDE

(*a*) *General.*—In attempting to find a suitable oxidizer for preparing the vanadium solutions for colorimetric determination, we tried hydrogen peroxide, and were thus led to the discovery of the reaction which is made the basis of the method we have finally adopted for determining vanadium in the phosphomolybdate precipitates. Much to our surprise, the peroxide, used in concentrated sulfuric acid solutions, acted as a reducing instead of an oxidizing agent, so that by its use we were able to easily reduce the vanadium quantitatively to the tetravalent stage. Moreover, we found by careful tests that the associated iron and molybdenum were never affected. We found that solid peroxides could also be used, but hydrogen peroxide is to be preferred, in general. The details of the reaction will be given fully in another paper and stated here only in so far as they apply to the method of analysis. To carry out the reduction, all that is necessary is to dissolve the phosphomolybdate-vanadium precipitate in concentrated sulfuric acid (filtration having been made on asbestos), add a few drops of nitric acid, fume strongly for two or three minutes, remove from the hot plate, allow to cool, and add hydrogen peroxide in very small quantities, with vigorous shaking after each addition, until the solution takes on a deep brown color (due to action on the molybdate); this always disappears on heating, and is followed by the clear green or blue color (depending on the ratio of V to Mo) of vanadyl vanadium. The flask is replaced on the hot plate and the solution fumed for a few minutes, after which it is cooled, diluted and titrated against permanganate. The whole operation is extremely simple, the end-point very good, and as our data show, the results are very accurate.

(*b*) *The Method.*—For steels containing vanadium, chromium, nickel, titanium, manganese, molybdenum, singly or in combination, dissolve an amount of drillings estimated to contain 2 to 10 mg. of vanadium in nitric acid (sp. gr. 1.135), boil till free from fumes, oxidize with permanganate solution, dissolve the manganese peroxide in sodium sulfite solution, and boil till free from fumes. In other words, prepare the solution exactly as for a phosphorus determination, examining any insoluble for vanadium. Nearly neutralize with ammonium hydroxide (0.96) and add an amount of sodium phosphate solution containing at least ten times as much phosphorus as there is vanadium present. Bring the solution to boiling, remove from the plate and add at once the usual necessary excess of the molybdate reagent to precipitate the amount of phosphoric acid added. Agitate for a minute or so, when it will be found that the precipitate settles rapidly. Filter the supernatant liquid by suction through an asbestos filter, and wash three times by decantation with hot acid ammonium sulfate solution, pouring the washing liquid through the filter. The last wash solution should be decanted off as completely as possible from the precipitate in the flask and the filter should be sucked dry. The rubber stopper carrying the filter is now fitted to a small, dry bottle, and hot, concentrated sulfuric acid is poured on the filter to dissolve the small amount

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[1] Gmelin-Kraut, "Handb. d. anorg. Ch.," 7th Auf., Vol. III, Pt. 2, p. 87.

[2] *Ztschr. anorg. Chem.*, **35**, 156 (1903).

of precipitate thereon. This dissolves quickly and the solution is drawn through by suction into the bottle. The contents of the bottle are transferred to the flask in which precipitation was made, and the bottle is washed once with concentrated sulfuric acid, the washings being added to the flask. For every 10 mg. of phosphorus present a final volume of 5 to 8 cc. of concentrated sulfuric acid is necessary. The contents of the flask are heated until solution takes place, a few drops of nitric acid (1:25) added and, when fumes are coming off strongly, the flask is removed from the plate and the vanadium reduced by successive small additions of hydrogen peroxide as above described. Replace on the hot plate, fume for four or five minutes, cover the flask, cool, dilute so as to secure an acidity of one part to five by volume, and titrate at a temperature of 70° to 80° C. against 0.01 N permanganate. The condition as to acidity and temperature must be closely observed in order to secure a satisfactory end-point.

For steels of the above classes containing tungsten, the only change necessary is to dissolve in aqua regia, dilute with hot water, filter off the tungstic acid, nearly neutralize with ammonium hydroxide, and add 10 grams solid ammonium nitrate for every 100 cc. of the final volume[1] before precipitating as above described. If desired, the tungstic acid on the filter may be dissolved in a small amount of sodium hydroxide solution (free from vanadium), acidified with nitric acid and tested for vanadium by hydrogen peroxide. We have not found vanadium here, and accordingly make no provision for its determination.

(*c*) *Solutions Necessary.*—Nitric acid of sp. gr. 1.135. Use 20–25 cc. for each gram of drillings to be dissolved.

Potassium permanganate for oxidations: 15 grams per liter.

Sodium sulfite: 50 grams per liter. A solution of sulfurous acid may be substituted.

Sodium phosphate: 124 grams $Na_2HPO_4.12H_2O$ per liter. One cc. contains approximately 10 mg. of phosphorus and will precipitate 1 mg. of vanadium. The solution may be standardized by evaporating a definite volume to dryness, igniting the residue and weighing the $Na_4P_2O_7$ so formed.[2]

Molybdate reagent: Make up according to the usual formula; 1 cc. will contain 0.05 to 0.06 gram MoO_3. For every mg. of phosphorus to be precipitated use at least 2 cc. of molybdate reagent. This ratio is used, however, only when precipitating large amounts of phosphorus. When precipitating small quantities of phosphorus 50 cc. of molybdate solution is the minimum volume used.

Acid ammonium sulfate: To 1000 cc. of water add 15 cc. ammonium hydroxide (0.90) and 25 cc. of sulfuric acid (1.84).[3] Use at a temperature of 80° C.

Potassium permanganate, 0.01 *N:* Standardize against sodium oxalate,[4] or, empirically, against a steel in which the vanadium has been accurately determined by other methods.

Peroxide: Hydrogen peroxide, 3 per cent. We have made our reagent with "Perhydrol." "Dioxygen" also proved satisfactory.

Table II shows a few of the very large number (in all nearly 400) of determinations made by us to be sure that the method is reliable. Nos. 16 and 17 of Table II are of interest as showing the delicacy of the method. As a matter of fact the vanadium can just as easily be concentrated from 50 or even 100 grams of steel or iron, so that excessively small percentages can be detected and determined with ease. Nos. 19, 20, 21 and 22 of the same table show the application to other materials, the results on the titaniferous magnetite ore being of special interest.

TABLE II.—RESULTS OBTAINED BY THE PEROXIDE REDUCTION METHOD.[1]

No.	Amount of sample. Grams.	Cr present. Mg.	P added. Mg.	V present. Mg.	V found. Mg.	V_2O_3 found. Per cent.
1	1	45	12	1.11	1.17	
2	1	180	20	1.92	1.91	
3	1	135	35	3.19	3.26	
4	1	90	45	4.52	4.60	
5	1	45	60	6.38	6.49	
6	1	225	100	10.64	10.73	
7	1	50	10	1.02	1.16	
8	1	100	25	2.54	2.58	
9	1	150	40	4.06	4.15	
10	1	200	50	5.08	5.07	
11	1	250	60	6.08	6.18	
12	1	50	80	8.13	8.40	
13	1	100	90	9.12	9.42	
14	1	150	100	10.15	10.22	
15[2]	5		19		0.995	
16	20		20	1.00	1.02	
17	20		19	1.11	1.24	
18	1		25	2.66	2.75	
19	2		19		1.07	0.078
20	10		39		3.41	0.05
21	10		19		0.66	0.01
22	10		19		0.81	0.012

If the expected content of vanadium in a sample is not known accurately enough for adding the necessary excess of phosphoric acid, two or more precipitations may be necessary.

We have found the arrangement shown in Fig. 1 useful for handling the concentrated sulfuric acid; it is much more convenient to use than a reagent bottle. It stands on a large sheet of glass. Also, the funnel with glass stopper shown in Fig. 2 is useful but not necessary. It is made by sealing a carbon filter to the inlet tube of a thick-walled glass wash-bottle, the latter being used as a suction filter flask.

[1] Except as otherwise indicated, the solutions used for these determinations were made by adding chromium and vanadium to the nitric acid solution of a vanadium and chromium-free steel in the proportions indicated in the table. The vanadium was added from an ammonium vanadate solution, which was standardized by reducing with sulfur dioxide and titrating against permanganate; the chromium was added from a chrome-alum solution, the chromium content being calculated from the amount of salt weighed out.

Nos. 1 to 6, and 15 to 22, inclusive, reduced with magnesium peroxide.

Nos. 7 to 14, inclusive, reduced with hydrogen peroxide.

[2] No. 15, B. S. Chrome-tungsten Steel Standard No. 30 (in preparation). (V found = 0.02 per cent.; not determined by any other method.)

No. 18 contained 23 mg. of titanium as titanium sulfate.

No. 19, B. S. Magnetite Ore Standard, No. 29.

No. 20, B. S. Manganese Ore Standard, No. 25.

No. 21, B. S. Sibley Ore Standard, No. 27.

No. 22, B. S. Crescent Ore Standard, No. 26.

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[1] Bureau of Chemistry, *Bull.* **107** (Revised), p. 3.

[2] Baxter, *Am. Chem. J.*, **28**, p. 301 (1902).

[3] Blair, "The Chemical Analysis of Iron," 7th Ed., p. 97.

[4] Bur. Stand., *Circular* **26**, 2nd Ed., p. 10.

If rubber stoppers are used, they should be good sound ones, so that pieces of rubber cannot drop into the concentrated sulfuric acid solutions.

The largest amount of vanadium determined in Table V (10 mg., or 1 per cent. on a one-gram sample) gives about as large a volume of precipitate as it is convenient to handle. We have precipitated and determined accurately as much as 27 mg. of vanadium, using the 10 to 1 ratio of phosphorus, but the manipulation in such cases becomes inconvenient. This is about the only serious limitation placed on the method, making it necessary, when dealing with large amounts of vanadium, to precipitate from an aliquot corresponding to a relatively small sample. For steels, alloys, ores, rocks, etc., containing from traces up to 5 or 6 per cent. of vanadium the method, we believe, can be used wherever phosphorus can be precipitated as phosphomolybdate from solutions of these materials.

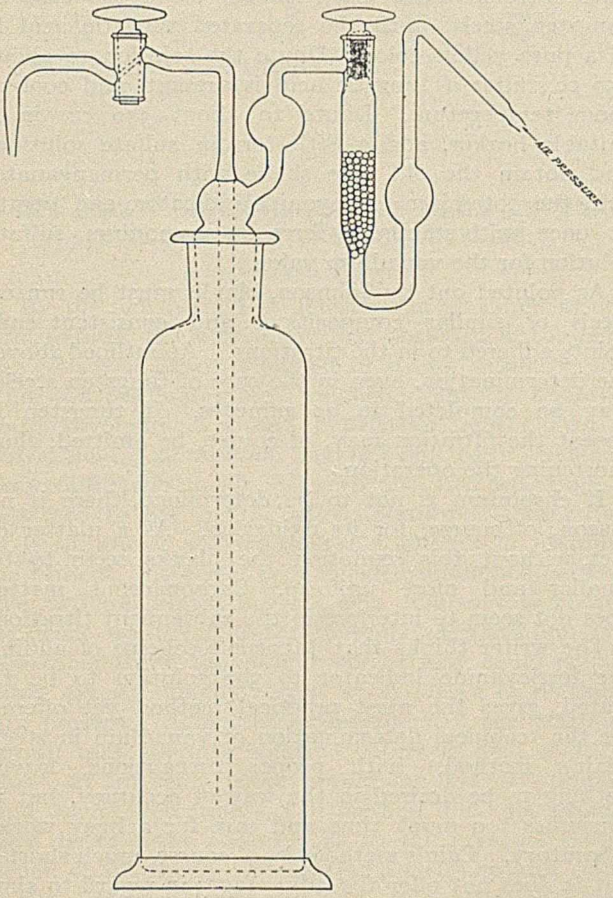

FIG. 1.

7. NOTES AND PRECAUTIONS.

The presence of vanadium in the phosphomolybdate precipitate is shown by the yellow to orange color of the cold, concentrated sulfuric acid solution of the precipitate, 0.05 mg. vanadium showing a perceptible color in a volume of 25 cc.

In carrying out the peroxide reductions it is necessary to use a flask instead of an open dish or beaker. If the latter is used there is reduction of the molybdenum where the strong solution acid "creeps" up along the sides of the vessel, the reduction showing by the development of an intense blue coloration.

If, after the addition of peroxide and subsequent heating, the vanadium is not reduced, it is probably due to traces of nitric acid in the solution, which may be removed by further fuming; the treatment with peroxide should then be repeated. In this connection we may note that nitrous fumes readily oxidize tetravalent vanadium and hence the reductions should be carried out in an atmosphere free from such fumes. After the reduction, it is advisable to cover the flask with a watch glass while the solution is cooling in order to prevent accidental introduction of organic matter.

If the final titration is carried out in acid of greater concentration than 1–2 by volume, the end-point is rendered uncertain because of the deep yellow color which the pentavalent vanadium, formed during the titration, gives with strong sulfuric acid. We recommend a dilution of 1–5, in which the end-point is very sharp.

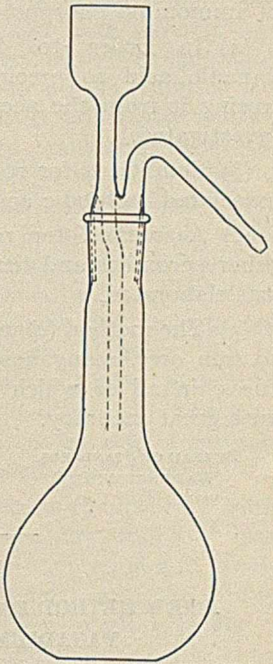

FIG. 2.

The time required for making a determination is worthy of note. Working with a vanadium steel, the sample was weighed out, dissolved and precipitated in 10 minutes, the precipitate washed and dissolved in sulfuric acid in 9 minutes more, while the reduction and titration required a further 12 minutes, giving the completed determination in approximately $^1/_2$ hour. By operating on a large number of samples at one time, the determination can be made as rapid, if not more so, than that of phosphorus in steels. We have frequently completed 20 determinations in less than 7 hours, even while giving much attention to uncompleted details. With these worked out the method should allow the completion of twice as many determinations in a day.

Manganese ores are readily decomposed with hydrogen peroxide in the presence of nitric acid. This solution is very well adapted for the determination of vanadium; the insoluble should also be tested.

When precipitating vanadium from a solution containing hydrochloric acid and, in general, when the volume of the solution is very great we recommend the addition of 10 grams of solid ammonium nitrate for every 100 cc. of solution.

8. SUMMARY.

(1) It was found that vanadic acid may be quantitatively precipitated by ammonium phosphomolybdate.

(2) The vanadium-bearing phosphomolybdate shows

different solubility relations compared with the normal phosphomolybdate, with respect to the usual washing solutions used in determining phosphorus.

(3) Conditions are given for quantitatively precipitating vanadic acid when in solution alone, or accompanied by a variety of other elements, by means of ammonium phosphomolybdate.

(4) In order to determine quantitatively the vanadic acid so precipitated, (*a*) the possibility of freeing it from the accompanying molybdic acid was investigated.

(*b*) Conditions for reducing it without reducing the associated molybdic acid were developed.

(*c*) A method for reducing it by hydrogen, and other peroxides and titrating it against permanganate was elaborated.

(5) The method (*c*) was applied to a variety of steels, to iron ores, manganese ores, and to synthetic mixtures, in all of which the vanadium was determined with great accuracy.

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A NEW METHOD FOR THE DETERMINATION OF VANADIUM; AN EXPLANATION.

By J. R. CAIN AND D. J. DEMOREST.

Received January 25, 1912.

The discrepancy in results obtained by us when using manganese dioxide, as mentioned in the paper on "A New Method for the Determination of Vanadium," page 249, led us to seek the cause. We exchanged samples of manganese dioxide and each found that the other's reagent behaved as stated in our respective papers. However, it was noted by Mr. Cain that Mr. Demorest's dioxide, which oxidized differentially, was much coarser than the manganese dioxide which the former had used, and which oxidized both the lower oxides of vanadium and iron. Upon grinding the coarse manganese dioxide very fine he found that it oxidized both iron and vanadium oxides as his own preparation had done. On the other hand, Mr. Demorest succeeded in separating a coarse portion from the manganese dioxide used by Mr. Cain which oxidized differentially.

Thus, the discrepancy is evidently due to a difference, in the two cases, of the velocities of the reactions:

$$(1)\ V_2O_4 + MnO_2 = MnO + V_2O_5$$
$$(2)\ FeO + MnO_2 = Fe_2O_3 + MnO$$

Mr. Demorest's reagent had a degree of fineness such that in the brief period of treatment the velocity of reaction (1) was inappreciable and reaction (2) was completed; whereas with material of the fineness used by Mr. Cain both reactions went to completion. The securing of such different results merely by changing the size of the grain of the reacting solid seems a matter worthy of further investigation.

THE RAPID DETERMINATION OF VANADIUM IN STEEL.

By FRANK GARRATT.

Received Dec. 20, 1911.

The writer has for some time used the following modification of Johnson's method[1] for determining vanadium in steel. Johnson's procedure is adhered to in all respects, except that the oxidation of the chromium and vanadium in hot, dilute sulfuric acid with potassium permanganate is omitted. With this omission the method is extremely simple and, briefly, is as follows:

Dissolve 2 grams of steel in about 50 cc. of dilute sulfuric acid; when solution is complete, oxidize the iron, and tungsten if present, by adding about 5 cc. of concentrated nitric acid to the hot solution. Boil until nitrous fumes are expelled, or in the case of tungsten steels, until the separated tungstic acid is of a pure yellow color. Dilute the solution to about 150 cc., filter if tungstic acid is present, and cool to room temperature. Dilute to about 350 cc. in a suitable beaker, add a little ferrous sulfate solution, and obtain the old rose shade with permanganate. Add the potassium ferricyanide indicator, and titrate at once with standard ferrous ammonium sulfate solution for the vanadium value.

As pointed out by Johnson, blanks must be run on steels of similar composition, and consistent end-points adhered to in the titrations. As outlined above, the determination, even in the case of tungsten steels, may be completed in 20 minutes. If tungsten is absent the filtration may, of course, be omitted, thus shortening the operation.

If chromium is not to be determined, there is no reason, of course, for its oxidation. As a matter of fact, without this oxidation the blanks seem to be smaller and more uniform. Carbonaceous matter does not seem to interfere in the subsequent titration.

The writer thinks that Johnson's scheme of adding the ferricyanide indicator to the solution to be titrated, gives the most practical method yet offered for the technical determination of vanadium in steel. Blair's method,[2] with proper precautions, leaves nothing to be desired in the way of accuracy, but it consumes too much time and care for a busy works laboratory. Cain's method[3] is, of course, much shorter but it does not offer the advantages in regard to simplicity and rapidity that Johnson's method possesses. Blair's and Cain's methods may well be considered desirable for standardizations and umpire determinations, but Johnson's method seems to be *the* one for routine work. If the procedure described herewith is adopted, the determination of vanadium is much simplified, and takes its place with the rapid methods for determining carbon, phosphorus, manganese, etc. Certainly the laboratory doing routine work on vanadium steels need not worry about its determination.

The following table gives some results obtained by this rapid modification. Some of the steels contained no chromium, while others varied from 0.90–6.00 per cent. The presence of chromium offers

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[1] "Chemical Analysis of Special Steels, etc.," p. 8.

[2] *J. Am. Chem. Soc.*, **30**, 1229.

[3] THIS JOURNAL, **3**, 476.

no complications, however, simply increasing the blank to be deducted from the ferrous ammonium sulfate used in the final titration.

	Per cent. V.			
No.	By Blair's method.	Added as NH_4VO_3.	Per cent. V by rapid method.	Difference by rapid method.
1	0.14	....	0.15	+0.01
2	0.25	....	0.25	none
3	0.47	....	0.45	—0.02
4	0.64	....	0.65	+0.01
5	0.89	....	0.88	—0.01
6	1.13	....	1.13	none
7	1.27	....	1.29	+0.02
8	1.31	....	1.31	none
9	1.37	....	1.37	none
10	4.67	....	4.68	+0.01
11	....	0.15	0.16	+0.01
12	....	0.50	0.50	none
13	....	1.00	0.99	—0.01
14	....	1.00	0.98	—0.02

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THE DIRECT DETERMINATION OF SMALL AMOUNTS OF PLATINUM IN ORES AND BULLION.[1]

By FREDERIC P. DEWEY.

By the old method of determining platinum in ores and bullion, the silver-alloy first obtained in the regular course of assay is parted in strong sulphuric acid and the residual metal weighed. This is realloyed with silver by a second cupellation and parted in nitric acid, the residual metal being again weighed. Any difference shown between the two weighings is assumed to be, and is called, platinum. Sometimes it is so, and if any considerable amount of platinum be present, there will be a decided difference between the two weighings; but a slight difference is no real evidence whatever of the presence of platinum. On the other hand, the second weight may equal or possibly exceed the first, even when traces of platinum are present. Again, other members of the platinum group may go into solution in nitric acid more or less. If present, these would be called platinum and escape detection. The method does not provide any direct tests whatever as to the presence or absence of platinum. It is often indecisive and sometimes gives erroneous results. It is, therefore, quite unsatisfactory.

Being called upon many times to determine platinum, in a wide variety of materials, particularly when present in very small amounts, I have realized the disadvantages and defects of this old method.

In an article on the solubility of gold in nitric acid,[2] I have briefly outlined a method of gathering a little gold out of a solution containing much silver, which furnishes the basis of an excellent method for the direct and absolute determination of small amounts of platinum and has the added advantage that the metal weighed may be subjected to suitable tests, to determine that it really is platinum, and to reveal the presence of other members of the platinum group.

In the regular course of assaying for the precious metals, gold is parted from silver by dissolving the silver in nitric acid. If platinum be present in small amounts only, it will readily go into solution in the nitric acid. If now a limited amount of hydrogen sulphide be added to the solution from parting, any platinum present will be precipitated as sulphide, along with some silver sulphide. On filtering off the precipitate (which generally is sufficiently washed by the operations necessary to transfer it from the precipitating dish to the filter), the moist filter is transferred to a small porcelain crucible, dried at a low heat, and burned off by gentle ignition. This transforms the sulphide precipitate into a metallic sponge, which is wrapped in a small piece of thin lead foil and cupelled. The resulting bead is then parted in strong sulphuric acid, when the platinum will be left as a dark residue, generally collected in spongy form, even when minute in quantity. This sponge, after reboiling in fresh acid, if necessary, is suitably washed by decantation, annealed, and weighed.

Generally, the final metal speaks for itself as being platinum, but, if there should be any doubt, it may be dissolved in a drop or two of aqua regia and gently evaporated. The solution obtained may be tested with potassium iodide, or a few small crystals of ammonium chloride may be added, when the characteristic precipitate will show itself. As a further test this may be filtered off and gently ignited to produce spongy platinum. If the amount of the final metal be considerable, the platinum may be determined by the double-chloride method. Any decided difference shown would indicate the presence of other members of the platinum group, for which direct test could then be made.

For precipitating the platinum and the necessary silver from the parting-solution, a very dilute solution of hydrogen sulphide should be used. One part of a strong solution should be diluted to from 10–20 parts with water. If the solution of silver nitrate be strongly acid, it should be largely diluted, or it may first be evaporated and then diluted. The very dilute hydrogen sulphide solution should be added very slowly to the silver nitrate solution with constant stirring. The solution is, of course, at once darkened, but there should be no immediate separation of a visible precipitate. The solution should be stirred occasionally, and in about 2 hrs. flocks of precipitate should appear. It may be filtered in from 3–4 hrs., but it is a good plan to let it stand over night if possible.

The amount of hydrogen sulphide required depends, of course, upon the amount of platinum present. If this should be roughly known or suspected, the amount used should generally be enough to precipitate the platinum and from three to five times as much silver. On an entirely unknown ore, I should at first use 1 cc. of strong hydrogen sulphide solution diluted to 15 cc., and reserve the filtrate from the sulphides for retreatment, if necessary. On an unknown bullion

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[1] Presented at the New York meeting of the American Institute of Mining Engineers, February, 1912, and published in the Bulletin of the American Institute of Mining Engineers, April, 1912, Serial No. 64.

[2] *J. Am. Chem. Soc.*, **31**, 323 (1910).

I should use 2 cc. of strong solution diluted to 30 cc., partly because bullions are liable to carry much more platinum than any ordinary ore, and partly because the volume of the silver nitrate solution from parting the gold must necessarily be larger. If, however, it is known that minute amounts of platinum are present, it is still necessary to use sufficient hydrogen sulphide to give a silver bead large enough to handle comfortably. For this reason I seldom use less than the equivalent of 1 cc. of strong hydrogen sulphide solution.

It may happen that the final metal shows the yellow color of gold, due to the fact that exceedingly fine float-gold passed over in decanting the solution of silver nitrate from the gold. In such a case the metal must be realloyed with silver and the treatment repeated. When the proportion of gold to silver in the metal being parted is so small that the gold separates in a very finely divided state, it will often save trouble to filter the silver-nitrate solution, to separate any float-gold, before adding the hydrogen sulphide.

This method has been used with the utmost satisfaction in determining very minute amounts of platinum in various silver-products directly. Much of our silver coinage, for instance, will show a few tenths of a milligram of platinum in 100 g. of coin. Recently I examined samples from two purchases of fine silver. Very large samples were dissolved in nitric acid. The acid in portions was poured upon the samples and allowed to act at a gentle heat until exhausted. Finally, a small amount of residual silver was removed from the solution and dissolved in a small amount of fresh acid, the solution being then united with the main solution, and the whole evaporated nearly to dryness. It was then diluted to about 250 cc. and 5 cc. of strong hydrogen sulphide solution diluted to 50 cc. was poured in with constant stirring.

This operation concentrated the gold and platinum of the silver into a small amount of sulphide precipitate. This precipitate was filtered off, roasted, and cupelled. The resulting bead was parted in nitric acid, and the gold determined. The silver nitrate solution was treated with dilute hydrogen sulphide solution, equivalent to about 1 cc. of strong solution, and the platinum parted from the silver by strong sulphuric acid.

These two samples yielded the following results:

No.	Silver taken. Gram.	Gold found. Milligram.	Platinum found. Milligram.
1.............	122.32	0.28	0.67
2.............	125.47	0.12	0.18

In case we have a material containing a considerable amount of platinum, the well known fact that platinum alloyed with silver is not entirely soluble in nitric acid must be considered. In such a case the gold from the first parting in nitric acid must be alloyed with silver and parted in nitric acid a second, or even a third time, before proceeding to precipitate the platinum from the parting solutions with hydrogen sulphide.

It is also very satisfactory to use the general method of gathering gold in a precipitate of silver sulphide in determining minute quantities of gold in high-grade silver, such as that produced by electrolytic refining. It is comparatively easy to gather the gold from very large samples of silver, up to 100 g. or more, into a decigram of silver, and then part by nitric acid as usual.

Probably this method of precipitating a noble metal in solution, or removing it from suspension in a liquid, by adding hydrogen sulphide in the presence of silver in the solution, could be used to advantage in determining gold in metallic copper and similar materials.

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THE DETERMINATION OF MOISTURE IN COALS.

By E. H. ARCHIBALD AND J. N. LAWRENCE.

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According to the official method for the determination of moisture in coal, the sample should be heated for one hour, preferably in a double-walled toluene bath, at a temperature of 104–7°, the loss in weight of the sample being taken as the moisture. It is of course recognized by many that the result does not necessarily represent the true moisture, but the magnitude of the error that may be made by following these directions does not seem to be appreciated. The following experiments were undertaken for the purpose of comparing the quantity of moisture which might be found according to the official method, with that which may be taken as representing the true moisture and thus ascertaining the magnitude of the errors which might be caused by oxidation of the coal, and evolution of gases at different temperatures, and the retention of the moisture by certain coals, which, being very porous, hold the water very tenaciously.

The work that has been done upon occluded gases in coal has a direct bearing upon this problem. Obviously, the more gas given off during heating, other things being equal, the larger the error which will be made. That carbon dioxide, oxygen, methane, nitrogen, carbon monoxide and ethane are evolved from peats and coals when heated, has been shown by Websky,[1] VonMeyer,[2] Thomas,[3] and a number of other investigators.

Parr and Baker[4] have shown that when coal is first mined it evolves hydrocarbons, chiefly methane, quite rapidly; but after a period of four months scarcely any methane is given off. Their data also show that carbon dioxide is evolved especially at a high temperature, and that oxygen is continually absorbed.

Porter and Ovitz[5] found that some coals dried in the air at 115° C. lose appreciable amounts of carbon

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[1] *J. prakt. Chem.*, **92**, 76 (1864).
[2] *Ibid.*, **5**, 144 (1872).
[3] *J. Chem. Soc.*, **13**, 793 (1875).
[4] *Univ. of Ill. Eng. Exp. Station, Bull.* **32**.
[5] *J. Am. Chem. Soc.*, **30**, 1486 (1908).

dioxide, and a great many take up oxygen. These authors have also shown that the coal absorbs oxygen without forming carbon dioxide.

E. E. Somermeier[1] has called attention to the fact that lignitic coals give up their moisture more slowly than harder coals.

Kent[2] has suggested heating the coal in an atmosphere of nitrogen, absorbing the moisture given off by means of calcium chloride, and determining the increase in weight of this drying agent, which should represent the true moisture.

N. W. Lord[3] notes that when finely ground samples of Illinois and Indiana coals were heated for different lengths of time, in different amounts, and under different conditions, practically all the moisture was expelled in the first thirty minutes; further that the change in weight represented not only the loss of moisture, but included any change due to oxidation, or other cause.

The recent work done by Porter and Ovitz[4] dealing with the subject in hand is most interesting. They were especially concerned with the volatile matter evolved from the coal at temperatures between 400° and 1100°. They also conducted a series of experiments for the purpose of weighing directly the moisture driven off from the coal at 105° when heated in a current of dry air or in nitrogen. The gaseous products were as far as possible collected and weighed. Their results show that a slight amount of carbon dioxide is produced by drying the Illinois and Wyoming coals at 105°, but only slight traces of hydrocarbons or carbon monoxide. Their experiments further showed that oxidation of the coal occurred to the extent of 0.4–0.5%, the amount of moisture obtained by absorptions in calcium chloride being greater, in almost every case, than the moisture determined by the official method.

The particular purpose of our work was to show the effects of heating the coal at different temperatures, for different lengths of time, and the extent to which a soft coal must be heated in order to expel the moisture. As will be shown below, the greatest error made in the determination of the moisture, by the official method, is likely to be due, not to oxidation or evolution of gases, but to the different rates at which moisture is expelled from different coals.

In the first set of experiments the coal was placed in a tube and heated in a stream of air free from moisture and carbon dioxide. After passing over the coal, this stream of air was led to tubes containing anhydrous calcium chloride.

The attempt was made to determine the amount of hydrocarbons given off, but this was not entirely successful. We can say, however, that the amount is exceedingly small below 110°; there seemed to be appreciable amounts at 120°.

After heating for an hour, or two hours, the tube containing the coal was weighed, giving the change in weight of the coal. Also, the calcium chloride tube was weighed giving the moisture driven out of the coal. The difference between the latter value and the gain or loss in the weight of the coal tube should give the value of the change due to oxidation, evolution of gases and such causes.

If gas was evolved along with the expelled water and some constituent of the coal oxidized at the same time, the change in weight will be negative or positive as the first two effects or the latter are the greater.

In making the weighings, glass tares were used, of very nearly the same volume and surface area, and containing the same amount of substance as the tubes to be weighed. The weights were carefully compared among themselves, and all corrections applied. The balance used was a long arm Becker which gave very constant results.

Blank tests were run frequently in order to assure ourselves that the air or nitrogen used was free from moisture, carbon dioxide, oxygen or any harmful impurity. These tests always gave very satisfactory results.

The experimental work may be classified as follows:

(1) The experiments with bituminous coal heated in a current of air.

(2) The experiments with bituminous coal heated in a current of nitrogen.

(3) The experiments with anthracite heated in a current of air.

(4) The experiments with anthracite heated in a current of nitrogen.

In the case of the first set of experiments the coal was heated at four different temperatures, *viz.*, 75°, 100°, 110°, and 120° starting with a fresh sample of coal for each temperature. Each sample was heated one hour, then weighed, heated two hours and again weighed; while in the case of a few samples the heating was continued for two hours and then for one hour. At each of these intervals the change in weight of the coal and the true moisture given off was determined, as well as the unsaturated hydrocarbons evolved, if any. The data obtained are shown in Table I, expressed as percentages of the original weight of the coal. A gain in weight is indicated by the letter G. A loss in weight by L. These letters are inserted only when the result is different from that indicated by the heading of the column.

The results show that at 75° the loss in weight of the coal corresponds very closely to the moisture expelled from the coal; that an appreciable amount of moisture remained in the coal after the first hour of heating; that practically no unsaturated hydrocarbons were detected.

At 100° the moisture weighed was 0.19% greater than the loss in weight of the coal during the first hour. The coal gained instead of losing in weight during the second and third hours. This shows considerable oxidation as it is enough to cause not only this increase in weight but to make up for the loss due to the evolution of any gases, which must have

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[1] *J. Am. Chem. Soc.*, **28**, 1630.

[2] "Steam Boiler Economy," by Wm. Kent, p. 351.

[3] *U. S. Geol. Survey Bull.* **323**, p. 18.

[4] *J. Am. Chem. Soc.*, **30**, 1485 (1908).

TABLE I.

Exp. No.	Loss in weight.		Total loss in weight (Average). Per cent.	Moisture weighed.		Total moisture (Average). Per cent.	Unsat. hydrocarbons.	
	1st hr. Per cent.	2nd and 3rd hrs. Per cent.		1st hr. Per cent.	2nd and 3rd hrs. Per cent.		1st hr. Per cent.	2nd and 3rd hrs. Per cent.
				75°				
1	1.43	0.14	....	1.46	0.17	....	....	....
2	1.56	0.09	....	1.56	0.08	....	....	....
3	1.45	0.12	....	1.46	0.20	....	....	....
Aver.	1.48	0.12	1.60	1.49	0.15	1.64	....	....
				100°.				
1	1.66	G 0.02	....	1.84	0.14	....	....	....
2	1.55	G 0.05	....	1.74	....	....	....	....
3	1.67	G 0.05	....	1.89	0.07	....	....	....
Aver.	1.63	G 0.04	1.59	1.82	0.10	1.92	....	....
				110°.				
1	1.65	G 0.09	....	1.89	0.12	....	....	....
2	1.73	G 0.05	....	1.84	0.04	....	....	....
3	1.65	G 0.09	....	1.85	0.13	....	....	....
Aver.	1.68	G 0.08	1.60	1.86	0.10	1.96	....	....
				120°.				
1	1.75	G 0.16	....	2.01	0.22	....	0.09	0.22
2	1.72	G 0.16	....	1.98	0.19	....	0.09	0.07
3	1.70	G 0.06	....	1.87	0.19	....	0.04	0.22
Aver.	1.72	G 0.13	1.59	1.95	0.20	2.15	0.07	0.17

taken place to some extent. Our method failed to detect any unsaturated hydrocarbons.

At 110° the moisture weighed was 0.18% greater than the loss in weight of the coal. The gain in weight of the coal during the second and third hours is greater than at 100° showing more oxidation. Another point worth noting is that an appreciable amount of the moisture remains in the coal after the first hour's heating at this temperature.

The results at 120° show the moisture weighed to be 0.23% greater than the loss in weight of the coal during the first hour. The oxidation during the second and third hours is appreciably more than for 100° at this temperature, and we have an appreciable amount of hydrocarbons evolved, but this is much more marked during the second and third hours.

The amount of moisture given off during the second and third hours is considerable, being about 10% of the total moisture. If we wish to obtain some idea of the oxidation we must add to the difference between the moisture weighed and the loss in weight of the coal (0.56%) the weight of unsaturated hydrocarbons found (0.17%) giving 0.73% of the weight of the coal, a value which must be low, as we know other gases, as well as hydrocarbons, are given off.

The results obtained by heating the coal for the fourth and fifth hours, and again for the sixth, may be briefly summarized. The coal tube continues to gain in weight, but the gain is much less than for the second and third hours. A small amount of hydrocarbons appears to be given off at 110°. The moisture weighed is almost negligible even at 75°. All that can be driven off at this temperature disappears during the first three hours.

It would appear therefore from these experiments with the soft coal that in the determination of moisture as usually carried out, a considerable amount of moisture is left in the coal—at least 10% of the total moisture. If however the temperature is raised until this moisture is expelled, an appreciable amount of hydrocarbons in addition to other gases will be driven off. Oxidation of some constituents of the coal takes place causing an increase in weight, which may be estimated at about 0.80% of the weight of the coal.

We pass now to the results obtained by heating the coal in a current of dry nitrogen. The nitrogen was prepared by passing air through ammonia water and then over heated copper. The results are tabulated as in the previous experiments.

TABLE II.

Expt. No.	Loss in weight		Total loss in weight (Average). Per cent.	Moisture weighed.		Total moisture weighed (Average). Per cent.	Unsatd. hydrocarbons.	
	1st hr. Per cent.	2nd and 3rd hrs. Per cent.		1st hr. Per cent.	2nd and 3rd hrs. Per cent.		1st hr. Per cent.	2nd and 3rd hrs. Per cent.
				75°.				
1	1.63	0.13	....	1.40	0.06	....	....	....
2	1.58	0.08	....	1.44	0.20	....	....	....
3	1.61	0.10	....	1.42	0.18	....	....	....
Aver.	1.61	0.10	1.71	1.42	0.15	1.57	....	....
				100°.				
1	1.93	0.01	....	1.74	0.18	....	....	....
2	1.89	0.08	....	1.76	0.06	....	....	....
3	1.87	0.03	....	1.74	0.14	....	....	....
Aver.	1.90	0.04	1.94	1.75	0.13	1.88	....	....
				110°.				
1	1.99	G 0.05	....	1.84	0.04	....	....	....
2	1.87	G 0.03	....	1.82	0.14	....	....	....
3	1.92	....	....	1.84	0.09	....	....	....
Aver.	1.93	G 0.03	1.90	1.83	0.09	1.92	....	....
				120°.				
1	1.94	G 0.01	....	1.90	0.23	....	0.10	0.36
2	1.93	G 0.03	....	1.90	0.03	....	0.10	0.22
3	1.89	G 0.01	....	1.84	0.09	....	0.00	0.03
Aver.	1.92	G 0.02	1.90	1.88	0.12	2.00	0.07	0.20

At 75° the loss in weight of the coal was 0.14% greater than the moisture weighed. A separate test made showed that 0.08% of carbon dixoide was evolved from this coal when heated.

The results for 100° show that the loss in weight of the coal during the first hour's heating was greater by 0.15% than the moisture weighed. During the second and third hours' heating, however, the moisture weighed is greater then the loss in weight of the coal. This suggests the synthesis of some water from the hydrogen and oxygen in the ooal. An appreciable amount of moisture is left in the coal after the first hour's heating.

The results for 110° show the same variations as those for 100°. The moisture weighed is still less than the loss in weight of the coal, but the difference is now very small. At 120° the total moisture weighed for three hours is slightly greater than the loss in weight of the coal. Doubtless an appreciable amount of gas must have been driven off; in fact the amount of heavy hydrocarbons is large enough to be detected. Oxidation must have taken place to a considerable extent. Water is still retained after an hour of heating.

If we assume that the difference between the loss in weight of the coal when heated in nitrogen, and when heated in air, represents the oxidation, we can express the oxidation for the first hour in percentage values of the moisture; as follows:

TABLE III.

	Per cent.
At 75°	8.72
At 100°	14.84
At 110°	13.44
At 120°	10.26

The moisture in the bituminous coal was also determined at the different temperatures in the official way, *viz.*, by heating one-gram samples in platinum crucibles for one hour. The results follow:

TABLE IV.

	Moisture, official method.		
Temp.	No. I. Per cent.	No. II. Per cent.	Total "moisture weighed" from Table I. Per cent.
75°	1.12	1.07	1.64
100°	0.95	1.01	1.92
110°	1.32	1.39	1.96
120°	1.25	1.29	2.15

The true moisture in the coal is therefore greater than the moisture found by the official method by 40% of the total moisture.

It appears from Tables I–IV that the moisture determination, as usually carried out, is in error from several causes: firstly, as shown in Table III, the value is too small by 14% of the moisture, due to an increase in weight of the coal, caused probably by oxidation, which is far from being balanced by the loss of occluded gases; and secondly, due to the water that still remains in the coal, which, considering Table IV, amounts to about 26% of the total moisture; the two errors combined amount to 40% of the true moisture.

We now come to the experiments with the anthracite coal. In the first place, we will consider the results obtained by heating the coal in dry air.

TABLE V.

	Loss in weight.			Moisture weighed.			Carbon dioxide.	
No. of Expt.	1st hr. Per cent.	2nd and 3rd hrs. Per cent.	Total loss in weight (Average). Per cent.	1st hr. Per cent.	2nd and 3rd hrs. Per cent.	Total moisture (Average). Per cent.	1st hr. Per cent.	2nd and 3rd hrs. Per cent.
1	2.60	0.07	....	2.63	0.07	....	0.23	none
2	2.57	0.07	2.65	2.64	0.10	2.72	No determination.*	
1	2.60	0.03	....	2.62	0.22	....	0.16	none
2	2.67	0.03	2.67	2.70	0.19	2.86	0.14	0.07
1	2.64	0.04	....	2.64	0.31	....	0.15	0.07
2	2.63	0.03	2.67	2.63	0.13	2.86	0.18	none
1	2.73	G 0.11	....	2.62	0.11	....	0.16	0.11
2	2.73	G 0.06	2.65	2.66	0.05	2.72	0.26	none

* Tare was broken during the run.

The carbon dioxide was determined for all the following experiments by absorbing the gas in potassium hydroxide solution. The further determination of the hydrocarbons was not attempted. As heretofore the results are percentage values of the original weight of coal.

It is noted that in the case of both coals the moisture weighed is greater than the loss in weight of the coal. The water is much more easily expelled from the anthracite coal, as it is almost entirely driven off during the first hour of heating, while with the soft coal this was not the case.

The next series of results was obtained by heating the anthracite coal in an atmosphere of nitrogen.

TABLE VI.

	Loss in weight.			Moisture weighed.		
Expt. No.	1st hr. Per cent.	2nd and 3rd hrs. Per cent.	Total loss in weight (Average). Per cent.	1st hr. Per cent.	2nd and 3rd hrs. Per cent.	Total moisture (Average). Per cent.
			75° C.			
1	2.77	0.02	....	2.48	0.05	....
2	2.77	0.01	....	2.41	0.06	....
3	2.74	0.01	2.77	2.45	0.00	2.47
			100° C.			
1	2.84	0.03	....	2.31	0.00	....
2	2.77	0.04	....	2.51	0.00	....
3	2.79	0.10	2.83	2.35	0.00	2.39
			110° C.			
1	2.81	....	....	2.64	....	....
2	2.76	....	....	2.61	....	....
3	2.86	....	2.81	2.64	....	2.62
			120° C.			
1	2.85	....	....	2.54	....	....
2	2.83	....	....	2.45	....	....
3	2.83	....	2.84	2.53	....	2.51

The moisture weighed is appreciably less than the loss in weight of the coal. The difference is about 0.31%, while the carbon dioxide given off according to the previous experiments was 0.23%. The difference between these values, or 0.08%, represents roughly the unidentified gases.

As was the case when the coal was heated in air, practically all the moisture is driven off during the first hour of heating. The amount of this moisture is almost the same for 75° as for 120°.

The analysis of the anthracite according to the official method gave the following results:

TABLE VII.

	Moisture by official method.		
Temp.	No. I. Per cent.	No. II. Per cent.	Total "moisture weighed" from Table V. Per cent.
75°	2.37	2.40	2.72
100°	2.30	2.37	2.87
110°	2.39	2.42	2.88
120°	2.40	2.40	2.72

The moisture as found by the official method is here only from 15% to 20% less than the moisture weighed.

The bituminous coal and the anthracite were both analyzed for iron, sulfur, volatile matter and ash. The results follow:

TABLE VIII.

Constituent.	Bituminous coal. Exp. I. Per cent.	Bituminous coal. Exp. II. Per cent.	Anthracite. Exp. I. Per cent.	Anthracite. Exp. II. Per cent.
Iron	0.65	0.55	0.48	0.58
Sulfur	1.02	1.07	1.15	1.18
Vol. matter	32.49	31.80	5.77	6.13
Ash	6.83	6.74	8.37	8.34

We see from these experiments that the greater oxidation in the case of soft coal could scarcely be due to the greater amounts of iron and sulfur present, as these constituents are present to almost an equal amount in the two cases. Rather, the greater oxidation must be due to the fact that the moisture is not so rapidly expelled from the soft coal.

The curves shown in Figs. A and B serve to indicate very clearly the general character of the results. The temperatures are plotted as abscissae and the per cent. of moisture as ordinates. The curves of Fig. A represent the results for the bituminous coal, those of Fig. B the results for the anthracite. The total decrease in weight of the coal during the first three hours, which is shown in curve I of Fig. A is practically the same for all the different temperatures, the curve being practically a straight line. Curve II shows the gradual increase in moisture given off by the coal as the temperature rises. Here too we have practically a straight line. Curve III represents the variation in the weight of the bituminous coal when heated for three hours at the different temperatures, in nitrogen. For temperatures above 100° the weight is constant. This curve lies throughout its whole length far above Curve I, showing the effect of oxidation when the coal is heated in air. The relation of the amount of moisture given off to the temperature when the coal is heated in nitrogen is set forth by Curve IV. The upper portion of the curve lies a little below Curve II. This could be accounted for by assuming the synthesis of a small amount of water from the oxygen of the air and hydrogen present in the coal.

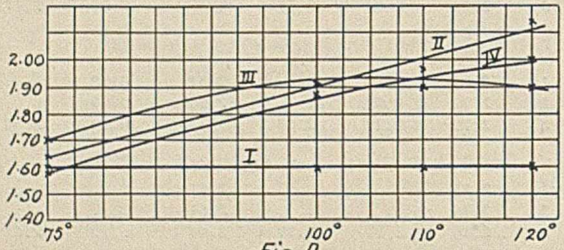

Fig. A

The curves for the anthracite (Fig. B) resemble in some respects those for the bituminous coal. Curve I, showing the relationship between the change in weight of the coal and the temperature at which it is heated (in a current of air), is a straight line, as in the case of the soft coal. The total moisture given off by the coal when heated in air shows a maximum at about 105° (Curve II). From Curve III we see that there is a continual loss in weight of the coal when heated in nitrogen, but this is not much greater for 120° than for 75°. Curve IV showing the moisture weighed at the different temperatures is more difficult to draw than the others as the results are not as regular. Obviously the result for 100° is worthless. However, for the sake of completeness the points are indicated.

The above considerations show that the errors made in the determination of moisture by the official method are much more serious in the case of bituminous coal than for anthracite. The determination being of little value in the former case, as at present carried out, we suggest that for this class of coals the method be modified, and that the coals be heated in a current of dry air at a temperature of at least 110°, the moisture given off being weighed directly after absorbing it by anhydrous granular calcium chloride. The results for one coal would then be comparable with those of another while at present this is not the case.

SUMMARY.

We may briefly summarize our results as follows:

(1) When the determination of moisture in coals is carried out according to the official method, the result is much lower than it should be, the error amounting in the case of some bituminous coals to 40% of the true moisture.

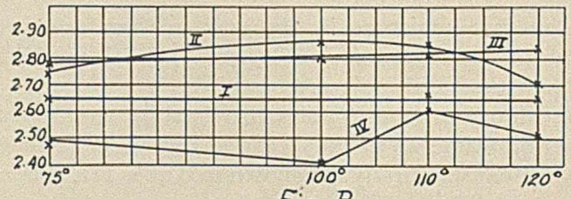

Fig. B

(2) The oxidation of iron or sulfur or both, and the non-expulsion of a considerable part of the water which probably accounts for the largest errors here involved, are much greater in the case of bituminous coal than with anthracite: due on the one hand to the moisture remaining in contact with the coal at a high temperature for a much longer time, and further to the more porous nature of the softer coal.

(3) It was suggested that for bituminous coals the method be modified and that the coal be heated in a current of dry air at a temperature of at least 110°, the moisture given off being weighed directly, after absorbing it in anhydrous calcium chloride.

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SYRACUSE UNIVERSITY.

A METHOD FOR THE UTILIZATION OF LEAD FURNACE FUME.

By L. S. HUGHES.

Received Dec. 18, 1911.

A large item of expense in the operation of lead smelting plants is the treatment of furnace fume. Where the so-called "open-hearth" furnaces are employed this by-product frequently amounts to more than twenty per cent. of the total ore charge and carries approximately that proportion of the original metallic values.

Ordinarily, "open-hearth" furnaces are arranged in a single battery below a common flue which receives the fume from all the furnaces. This flue delivers into a series of collecting chambers in which the furnace dusts and ashes are deposited. The fan which supplies the necessary draft is placed beyond these chambers and the fume proper is forced by its exhaust into a cloth filter system of the bag room type which retains the solid fume and filters it from the furnace gases. From the filter bags the fume falls into a closed brick chamber and is allowed to accumulate there until it is several feet in depth. The pile is then set on fire and slowly smolders until the sulfide and carbonaceous ingredients are oxidized. This burning occupies several days and in order to avoid interruption of the furnace operation several independent filter systems are used so that any one may be cut off whenever it is necessary to burn the fume therein. When it is finished the fume is converted into a whitish cinder of approximately the following composition.

	Per cent.
Lead sulfate	55
Lead monoxide	44
Zinc oxide	1
Ferric oxide	traces

If a sufficient settling system has been employed between the furnaces and the bag room there will be no more than traces of the non-volatile constituents of the furnace charge.

Hitherto no better means of disposing of the burned fume has been devised than that of using it as a smelting material: most commonly by reduction in a blast furnace, but occasionally in an open-hearth furnace. Attempts have been made to use the unburned fume as a pigment and there is a small market for it in the paint trade, but its variable color and certain difficulties in its manipulation sharply limit the demand and the total tonnage thus consumed is too small to affect the problem.

The remarkable freedom of the fume from non-volatile impurities and the fact that it represents a mixture of almost absolutely pure oxidized lead compounds after burning, presented it as a promising raw material for conversion into lead compounds, but the problem proved by no means easy of solution.

An examination of the literature disclosed several processes devised for the conversion of lead sulfate into other compounds in the wet way. Some of these were manifestly worthless from a commercial standpoint as the inventors had proceeded with a reckless disregard of the cost of reagents: others, which appeared to be conceived in a spirit of practicality, were carefully checked experimentally.

While it was desired to find a plan which would yield a product of lead oxide or hydrate, compounds not only merchantable *per se*, but readily convertible by ordinary processes into an indefinite number of compounds, methods for the direct conversion of the sulfate or sulfate-containing mixture into compounds of special desirability, such as the chromates, were included in the list of possibly available methods.

Prior methods proved disappointing in every instance, and in some cases a most grievous discrepancy developed between the facts, as revealed by experiment, and the statements published. Even where the methods had been the basis for patents, instances were found which strongly indicated that the claimants had neglected empirical verification of their ideas.

Attempts were made to convert the pulverized cinder directly into lead chromate by treatment with a soluble chromate, but the products proved of unsatisfactory composition through the persistence of a portion of the lead sulfate and in all cases were of unsatisfactory color and tinctorial strength.

Digestion with sodium hydrate and carbonate as a preliminary step gave but slightly better results as it proved practically impossible to convert all the lead sulfate present.

As the amount of residual sulfate appeared larger when a coarsely pulverized cinder was employed, a microscopic examination of the digested fume was made, and this showed plainly that the residual sulfate was encysted by crusts of hydrate, the complex particles having much the structure of a nut with a kernel of unchanged sulfate and a shell of hydrate. This observation naturally suggested trituration as a means of effecting complete conversion and the employment of a closed ball mill entirely obviated this difficulty, conversion being rapidly and completely accomplished.

Up to this point little attention had been paid to the amount of reagents employed but for commercial application it was manifestly necessary that the treatment be systematized and the chemicals reduced to the minimum amount. "Soda lye" had been selected as the most generally desirable reagent for decomposition of the lead sulfate, both because of its low cost and because by adding it in dry form its heat of solution within the mill obviated any necessity for the employment of extraneous heat to accelerate reaction. In order to obtain a sufficiently high temperature and also to yield a sodium hydrate solution of sufficient concentration the water was proportionately reduced. A mechanical difficulty appeared in the first test: the solution of sodium sulfate resultant from the decomposition was supersaturated and the crystals of sodium sulfate interlaced the paste of lead hydrate converting the entire mass into a tough, coherent cake which had to be broken out of the mill by hand. From a practical standpoint it was impossible to remove it by solution of the sodium sulfate by treatment with water, for the cake was almost impermeable by water. It was noted that this solidifying action did not take place so long as the mill was in motion, but immediately after it came to rest the setting occurred. Repeated efforts were made to introduce water immediately after grinding had stopped, but in every instance the "setting" had taken place.

The solution of this difficulty was effected by introducing a new pattern in double cone ball-mills which permitted of the introduction of water and washing out of the charge without stopping the mill. The body of the mill was of the familiar type employed in horizontal mills, but the outlet was made considerably wider than the charging hole so that when the level of water within the mill was raised it would overflow at the outlet only. This proved of the greatest convenience and value in operating. After conversion was completed a jet of water was turned into the charging hole and the rotation of the mill continued. The hydrate in the form of an impalpable sludge was, of course, kept continually stirred up and was rapidly floated through the outlet into a washing vat. This water-floating action had the additional advantage that by no possibility could any portion of the charge escape from the mill before it was reduced to extreme fineness.

Washing was effected by decantation and the hydrate was then ready for conversion into other compounds.

For conversion into chromate it was dropped from the washing vat into a large percipitating vat and treated with the theoretical amount of acetic or nitric acid required for its conversion into a basic salt; water was added and the necessary solution of an alkaline chromate or bichromate. The extreme reactivity of the hydrate enabled the conversion to be effected without heating and with no more than the theoretical amount of acid.

For the production of oxides the hydrate was pumped into a filter press and the cakes furnaced without previous drying.

It was found possible to produce a good lead arsenate at a considerably lower cost than obtains with present processes by mixing the freshly made hydrate with a solution of arsenic acid obtained by oxidation of arsenious anhydride with nitric acid, and boiling. The reaction was a little slow but the product most satisfactory.

Other instances of easily obtainable compounds might be cited but the possibilities of lead hydrate are manifest.

While the method offers absolutely nothing new from a chemical standpoint, it promises to have a very considerable influence upon the lead pigment business on account of the great economy over present methods which it entails. The degree of saving effected by using a by-product such as "blue fume" and thus saving both the smelting cost of producing pig lead and the additional cost of furnacing the pig lead to litharge and pulverizing the litharge is apparent from the following tables:

The cost of producing chrome by present methods varies somewhat according to the market rates for litharge, acetic acid, nitric acid and sodium bichromate; the following figures represent usual costs in manufacturing on a large scale:

Cost per cwt.

69 pounds litharge at 5½ c.	$3.79
43½ pounds 56% acetic acid at 3½ c.	1.38
46 pounds sodium bichromate at 5½ c.	2.53
Labor	0.25
Water and fuel	0.05
Packages and packing	0.25
	$8.25

To this must be added freight and selling expense.

These figures are based on good practice without waste. Most manufacturers compute their cost of production at from $8.50–$8.75. For small producers who have to buy in small lots and at higher prices the cost is much higher.

COST OF PRODUCING CHROME UNDER NEW PROCESS.

Using the same basis of prices as before, the cost per cwt. is:

11 pounds caustic soda at 2 c.	$0.22
80 pounds burned fume at 2½ c.	2.00
29 pounds 56% acetic acid at 3½ c.	1.38
46 pounds sodium bichromate at 5½ c.	2.53
Labor	0.25
Water and fuel	0.05
Packages and packing	0.25
	$6.68

To this must be added freight and selling expense.

It will be observed that less acid is used than in the former statement. This is because of the much greater reactivity of lead hydrate as compared with litharge. The burned fume is valueless except as a smelting material: its value is therefore the value of the metal which can be recovered from it, less the smelting cost and freight.

A METHOD FOR TESTING OUT PROBLEMS IN ACID PHOSPHATE MANUFACTURE.[1]

By F. B. Porter.

Received Jan. 12, 1912.

The process of manufacturing acid phosphate is, like many other factory processes, very hard to carry out on a laboratory scale. The writer has at various times made attempts to do this on 1000 or more grams of rock dust.

It has so far been practically impossible to stir sufficiently and control the temperature well enough with the limited apparatus available to get satisfactory results.

This being the case we recently devised the plan of using the quantities of acid and rock required to make 2 grams of finished acid phosphate, stirring them together with a stirring rod in a test tube and using the entire product for the insoluble test.

The following is the method in detail: Weigh 1.100 grams of rock dust into a 5" × 5/8" test tube, add the quantity of acid required from a small bore 1 cc. Mohr's pipette, allowing the pipette to run empty and draining for a definite length of time (1 minute).

The acid required and used is determined by titrating amounts delivered in the same way with half-normal alkali.

Stir the acid and rock together for 3 minutes, being careful to see that the dust is all wetted by the acid in the first half-minute of the stirring period. The test tubes thus prepared, without removing the stir-

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[1] Presented at the forty-fifth meeting, American Chemical Society, Washington, December, 1911.

ring rod, are then held at any temperature for any time desired.

The resulting acid phosphate is transferred to a 9 cm. filter paper with water and the citrate-insoluble phosphoric acid determined by the Official Method. Page 3, *Bull.* **107,** Rev. Bureau of Chem.

At first this method gave occasional erratic results but with practice and care we are now able to get results agreeing practically within the limit of error of the citrate-insoluble method. The results used in this kind of work are averages of three and in most cases four separate analyses. In this way accurate reliable results are obtained.

This method has many advantages over one using larger quantities of rock. Three of these are:

1st. Large numbers of tests can be carried out with inexpensive apparatus common to every laboratory.

2nd. The temperature at which the tests are held can be easily and accurately controlled.

3rd. A large number of these tests can be made in the time required for one by any other method known to the writer.

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ATLANTA, GA.

ON THE DETERMINATION OF CARBON DIOXIDE IN SOILS.

By LEON T. BOWSER.

Received October 26, 1911.

Up to a comparatively recent time no method had been so thoroughly tried out as to be considered a reliable one for small amounts of carbon dioxide in soils. In 1908, the Association of Official Agricultural Chemists took up the matter of testing the applicability of the Knorr method, and in 1909 a still larger amount of coöperative work was done. The results of the work will presently be presented in tabular form.

The method outlined in the author's previous paper[1] having been found to yield good results with materials containing a large percentage of carbon dioxide, it remained to be seen whether it would be as satisfactory in cases where the percentage is small. As a preliminary, two determinations were made in a sort of artificial soil containing a known amount of carbon dioxide. A very pure sea sand was ignited for some time to remove all organic matter and decompose such calcium carbonate as might be present from finely divided particles of sea shells and other carbonate materials. This was cooled, and to a weighed portion was added enough analyzed $CaCO_3$ to give exactly 0.05 per cent. CO_2. A blank determination was first made on the water, reagents, and freshly ignited sand; then two determinations were carried out on the artificial soil. The blank first found was deducted from the titration results, and CO_2 calculated from the difference. The determinations gave 0.043 and 0.048 per cent. CO_2, an average of 0.0455 as against the 0.05 per cent. actually present, which seemed very satisfactory.

There was available a considerable quantity of each of the two samples for the 1909 A. O. A. C. soil work, and as the average of results from a large number of independent workers is likely to be somewhere near the truth, it was thought that here was an unusually good opportunity to compare the two methods. Four determinations were accordingly made on each of the two soils, under conditions parallel to those used by the A. O. A. C. workers, and the results are presented in Table I, accompanied by the Association results on the same.

TABLE I.

Soil 1.

	Knorr method. Analyst.							Volumetric method.
	1.	2.	3.	4.	5.	6.	7.	
	0.070	0.085	0.072	0.092	0.092	0.080	0.074	0.080
	0.073	0.082	0.073	...	0.085	0.074	0.080	0,077
	0.065	...	0.075	...	0.085	0.080	...	0.075
	0.072	...	...	...	0.082	0.080	...	0.084
	0.068	...	...	...	0.085	...	...	...
	0.073	...	...	...	...	...	...	...
Av.	0.070	0.083	0.073	0.092	0.086	0.079	0.077	0.079

General av. 0.078

Soil 2.

	Analyst.							
	1.	2.	3.	4.	5.	6.	7.	
	0.027	0.027	0.023	0.027	0.027	0.036	0.026	0.026
	0.028	0.035	0.021	...	0.027	0.036	0.025	0.031
	0.031	0.028	0.023	...	0.030	0.030	...	0.031
	0.024	0.035	0.020	...	...	...	...	0.026
	0.027	...	0.022	...	...	...	...	...
Av.	0.027	0.031	0.022	0.027	0.028	0.034	0.025	0.028

General av. 0.028

Comparison of Averages.

	Soil 1.	Soil 2.
A. O. A. C.	0.078	0.028
Volumetric..........	0.079	0.028

The averages given in the Association report are: No. 1, 0.081 per cent.; No. 2, 0.027 per cent. CO_2, but these include only the results of the first five analysts, the latter two reporting too late to be included. For the present work all of the results are considered, increasing the probability that the averages are near the truth. The agreement between these revised averages and the ones obtained by the volumetric method is remarkably close, and shows that the latter is thoroughly reliable. On the score of consistent results, the volumetric method is superior to the gravimetric. Thus on Soil 1 the A. O. A. C. results range from 0.065 to 0.092, a variation of 0.027 per cent., while the volumetric results range from 0.075 to 0.084, a variation of 0.009 per cent., or just one-third of the former. On Soil 2, the A. O. A. C. results run from 0.020 to 0.036, a variation of 0.016 per cent., as against 0.026 to 0.031, a variation of 0.005 per cent. for the volumetric, which, as with Soil 1, is practically one-third as great a difference.

The method followed was as outlined in the preceding paper,[1] and in each case 10 grams of soil were taken. Soils containing 0.1 per cent. or less of CO_2 require for titration an acid of strength not exceeding $N/50$, since when stronger acids are used the evolved CO_2 is equivalent to but a fraction of one cc., and too

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[1] THIS JOURNAL, **4**, 203–205 (March, 1912).

[1] THIS JOURNAL, **4**, 203.

great an error is thus introduced. Occasion may even arise where a centinormal acid is demanded, although the writer has never encountered such a case. Even with $N/50$ acid a considerable amount of care is necessary in observing end points, and the use of comparison solutions is advisable.

There are many ways in which this method seems especially adapted to soil work. Thus boiling the sample in the flask does not cause even the slightest bumping, and the evolved gas comes off smoothly and uniformly. Also, the vigorous boiling possible in this form of apparatus insures a thorough and constant stirring up of the sample, with consequent complete decomposition of the carbonates. One precaution which must be carefully observed, however, is in regard to the degree of heat applied to the flask at first. Just as the contents are about to begin ebullition there is a tendency to froth, and the flame should be turned down low for a moment until the solution is in full boiling.

A curious fact has been noted by several analysts in connection with the amount of a soil sample which should be introduced into the decomposing flask; results with 10 grams of soil are almost invariably higher than those with larger amounts. This is illustrated in Table II, where three independent analysts have obtained results decidedly similar.

Table II.

	Soil 1.			Soil 2.			
	50 gms.	35 gms.	10 gms.	50 gms.	40 gms.	20 gms.	10 gms.
Analyst 6	0.065	...	...	0.021	...	...	...
Analyst 7	...	...	...	...	0.025	0.0225	...
A. O. A. C. Av.	...	...	0.078	...	...	...	0.028
L. T. Bowser	...	0.061	0.079	0.025	...	...	0.028

An investigation into the causes of this behavior might yield results of considerable value.

Judging from the results secured, the titration method is apparently superior to the procedures now in use for the determination of carbon dioxide in soils. It is far more accurate, the manipulation simpler, results more uniform, and the apparatus itself not in the least fragile. These advantages, coupled with the fact that there are very few precautions to be observed, should make it of great service in the analysis of soils.

In conclusion, the writer desires to acknowledge his indebtedness for many favors to Mr. J. W. Ames, of the Ohio Agricultural Experiment Station, Mr. W. F. Pate, formerly of the same place, and Dr. A. M. Peter, of the Kentucky Station.

THE PHENOMENON OF THE APPARENT DISAPPEARANCE OF THE HIGHER BOILING PHENOLS IN CREOSOTED WOOD AND ITS EXPLANATION.

By Samuel Cabot.

Received January 18, 1912.

One of the mysteries of the chemistry of wood preservation is the apparent disappearance of the phenols from timber impregnated with coal tar creosote. The generally accepted explanation has been that carbolic acid and the cresols are volatile and soluble. Most authorities have been content with this explanation. From the logic of the fact, however, it does not seem to cover the more complex members of the series. Some of those found in creosote are non-volatile without decomposition under ordinary pressure and have been carried over into the distillate by the oil. These phenols are also less soluble than the bases which are found in old treated timber. In an earlier article it has been shown that the phenols are, if anything, less subject to evaporation than the oil fraction in which they are contained.

The only solution to their apparent disappearance would seem to be that they have been so altered in the process of time that they no longer can be found by the regular method of analysis. In accordance with this theory, experiments were conducted with a view of following and detecting the changes in the phenols of a high-boiling oil on exposure to the air.

First, the freshly distilled oil containing 7.2 per cent. of tar acid was exposed. It changed with considerable rapidity from a clear reddish color to a brownish black. The same oil with the phenols removed changed very slightly.

On extracting the tar acids from the blackened oil in the ordinary way with dilute caustic soda, it became much lighter in color and a black tarry layer separated out between the oily and aqueous liquids. This tarry substance was insoluble in benzole and only very slightly soluble in water, though readily so in acetone.

On weighing the phenols and tarry matter the results showed phenols, 6.77 per cent.; tarry matter, 0.47 per cent. The original freshly distilled clear oil when shaken with caustic soda precipitated no tarry material.

In the next tests some high-boiling tar acids were exposed on a watch glass for six months. The original phenols were entirely soluble in benzole. Those that had been exposed to the air, however, were only partially so, though readily soluble in acetone. A portion of that soluble in benzole was re-exposed for a period of two months. Again it became partially insoluble. The rest was analyzed for phenols in the usual way. It precipitated a tarry layer with caustic soda equal to 53% of its weight; the remaining 47 per cent. were recovered from the acidified liquid. The tarry products from both these experiments had a sharp acid taste much stronger than that of the oil. This tarry substance is curious in its behavior. A portion of it, while insoluble in caustic soda solution is soluble in water, resembling in this respect a soap. After the water-soluble portion has been washed out, some of the remainder becomes soluble again in the original oil or benzole. This can be partially, though not completely reprecipitated by the alkali. The remainder which is insoluble in either water or benzole is not changed in this respect by neutralizing with acid.

It would appear from these facts that the phenols go through three stages of oxidation: (1) To a product insoluble in a 10 per cent. alkali solution, but soluble as an alkali salt in water. (2) Being further oxidized to a product which will form a salt with an alkali, but hydrolyzes on dilution; in other words, stable only in an excess of caustic soda. (3) The end product with a very slight affinity for caustic soda, probably held in solution in the oil only by the unchanged and partially changed phenols. The original tarry matter on being heated cokes very easily, losing only about 15 per cent. of its weight.

The methods used to extract the oil from impregnated timber for analysis have been, so far as I have been able to find out, to treat (1) with benzole, (2) with toluole, (3) with ether, and (4) with absolute alcohol.

It will be noted that the first three methods could not extract the final oxidation product of the phenols, whereas the last one could. Nevertheless, the extract from the last method would show only a trace of phenols by the ordinary test because the common practice of distilling the oil before analysis would coke or decompose the oxidized phenols.

An extraction was made of some chips from the surface of a creosoted tie which had been in the ground from 1879 to 1906 and exposed to the air from then until 1911. Twenty grams of this wood completely extracted with benzole gave 0.78 gram of oil. This was redissolved in benzole and extracted with caustic soda. It gave a trace of phenols and 0.014 gram of tarry matter, or about 1.8 per cent. on the oil. The wood was then extracted with acetone. It gave 0.63 gram of a black, pitchy mass, a small portion of which was soluble in ether, but the whole readily soluble in absolute alcohol. It was slightly soluble in caustic soda, giving a yellowish coloration and a distinct, pyridine smell. It was sharp to the taste, resembling coal tar. On heating, it gave off a small amount of pungent gas, the remainder turning to coke.

This acetone extract probably contained some phenolic and basic products and some oxidized hydrocarbons, and a slight amount of resin dissolved from the wood.

The above experiments seem to show that the higher coal tar phenols will not volatilize from creosoted wood, but remain as more complex oxidation products insoluble and non-volatile in character and presumably with good antiseptic qualities, though whether these have been impaired or improved by the change is yet to be determined. At any rate, these oxidized phenols would seem to have to a considerable degree the three properties of prime importance in a wood preservative, namely, non-volatility, antiseptic qualities and insolubility.

LABORATORY,
SAMUEL CABOT, INC.,
BOSTON.

THE FLUIDITY OF FISH OIL MIXTURES AS AN ADDITIVE PROPERTY.

By GEORGE F. WHITE.

Received December 4, 1911.

The increasing adulteration of vegetable oils by fish oils as well as the substitution of one fish oil by another, has called forth many attempts to detect such practices in recent years. In many instances the chemical properties of the two oils so closely approximate each other that the ordinary commercial methods of analysis fail to distinguish either in a mixture of the two. Thus, it is known that dogfish liver oil may be offered as a substitute for cod liver oil without danger of discovery, especially when the oils are refined. Ordinary cod oil, used to a large extent for such purposes as currying, frequently consists of nothing but dogfish, shark, hake, or polluck oil. Menhaden oil is often used to replace whale and cod oils.

In order to definitely establish the fact that a certain sample of oil is a mixture, a great number of tests must be made, and, of course, these are of value only as they are accurate enough to detect small amounts of one oil in the other. A great quantity of data has been published on the viscosity of oils, from which many conflicting and erroneous conclusions have been drawn with respect to the connection between this physical property and the composition of the oil investigated. Thus Kessler and Mathiason,[1] in a paper "On the Interpolation Method of Oil Analysis," in discussing the properties of oil mixtures, state that "neither the viscosity nor the fluidity of such solutions are necessarily additive, even though there is no evidence to indicate that either chemical or molecular compounds are formed." This statement is directly contrary to the views of Bingham[2] who believes that the fluidity of a mixture of two liquids, which do not react chemically with each other, is the sum of the partial fluidities of the components.

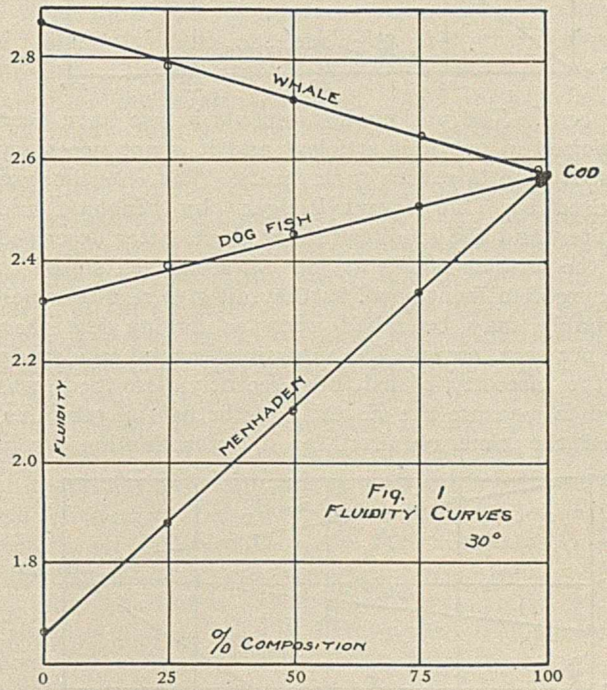
Fig. 1 Fluidity Curves 30°

The object of this investigation was to test the above theory by mixing various fish oils with each other in definite proportions by weight and studying

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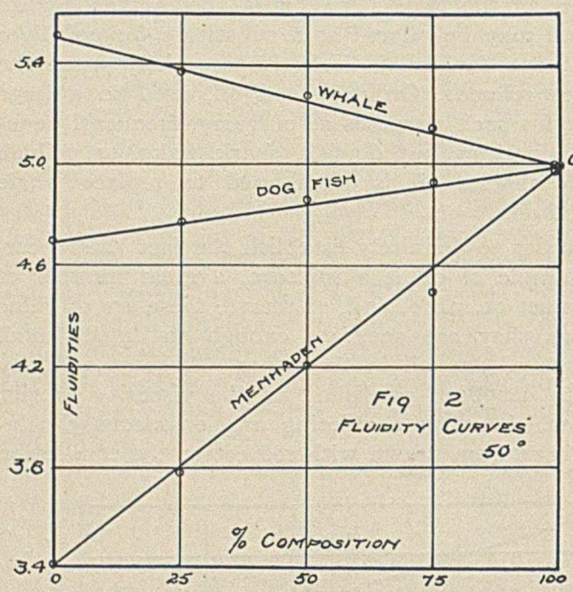
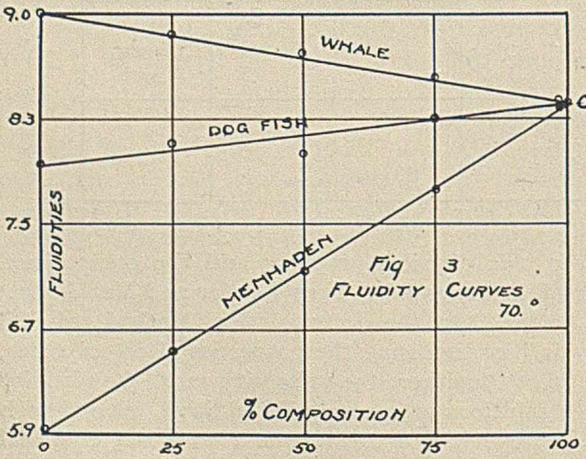
[1] THIS JOURNAL, 3, 66 (1911).

[2] *Z. physik. Chem.*, 66 1 (1909).

any relations between composition and viscosity or fluidity which might become evident.

The correct relationship between viscosity and composition can be established only by use of a viscosimeter which shall be accurate to at least one per cent. The various instruments in use have been criticized in previous articles[1] and it is not necessary at this time to review their faults. The viscosimeters devised by Thorpe and Rodger,[2] by Bingham and White,[3] and the modification of these latter described by the author of this article[4] all seem well suited to the problem mentioned, as they all give results which probably may be relied upon as having less than 0.2 per cent. error. The viscosimeter used in a study of the viscosity of fish oils recently described[5] was used to measure the viscosity of the fish oil mixtures, since the time required for a determination (from two to six minutes) was the most favorable for accurate work.



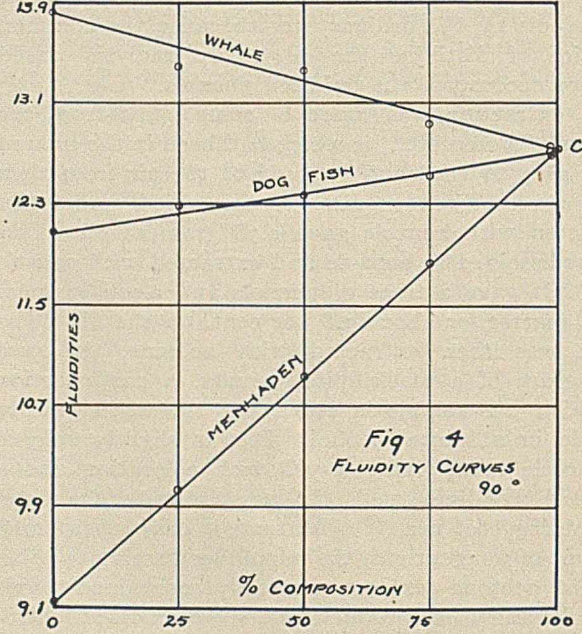


The whale and white cod liver oils, which were taken for use in this investigation, were commercial samples, while the menhaden and dogfish (Mustelus canis) liver oils were extracted from fish obtained at Woods Hole according to the previously described method. The mixtures were made up by weight and allowed to stand at least twenty-four hours before analysis, to secure complete homogeneity. Following is a table giving a few of the common constants obtained, the saponification and acid numbers being expressed as the number of milligrams of potassium hydroxide required for one gram of oil.

TABLE I.

Oil.	Cod liver.	Whale.	Menhaden.	Dogfish liver.
Iodine No. (Hübl).....	142.60	156.60	128.10	135.90
Saponification No......	185.80	192.80	16.26	193.00
Acid No..............	1.82	6.60	6.83	0.94

In the tables below are given the results of viscosity determinations expressed in absolute units, together with the fluidity calculated from the average viscosity.



Specific-gravity determinations of the pure oils were made in a pycnometer, no measurements being taken on the mixtures as the densities of these are nearly enough additive to allow proper calculation of the small kinetic energy correction $\frac{vd}{8\pi tl}$ in the following formula, used to obtain the viscosity values

$$\eta = \frac{\pi r^4 pt}{8vl} - \frac{vd}{8\pi tl}.$$

η is the viscosity, l the length and r the radius of the capillary tube, d the density of the oil, and v the volume of oil passing through the tube; p is the pressure to which the oil is subjected, and t is the time of flow.

TABLE II.—COD LIVER OIL.

Temp.	Viscosity.				
Degrees.	Rt. limb.	L. limb.	Av.	Fluidity.	Sp. gr.
30	0.3886	0.3882	0.3884	2.575	0.9277
50	0.2001	0.2005	0.2003	4.992	0.9149
70	0.1187	0.1189	0.1188	8.396	0.9008
90	0.07862	0.07882	0.07872	12.710	0.8900

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[1] *Biochem. Z.*, **37**, 482 (1911); THIS JOURNAL, **4**, 106 (1912).

[2] *Phil. Trans.*, **185A**, 307 (1894).

[3] *J. Am. Chem. Soc.*, **33**, 1257 (1911).

[4] See Note 2.

[5] THIS JOURNAL, **4**, 106–107 (1912).

TABLE III.—DOGFISH LIVER OIL.

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.	Sp. gr.
30	0.4319	0.4319	0.4319	2.315	0.9185
50	0.2133	0.2138	0.2136	4.682	0.9057
70	0.1262	0.1259	0.1261	7.931	0.8932
90	0.08272	0.08293	0.08283	12.080	0.8796

TABLE IV.—MENHADEN OIL.

30	0.6012	0.6025	0.6019	1.661	0.9371
50	0.2936	0.2938	0.2935	3.407	0.9234
70	0.1683	0.1683	0.1683	5.945	0.9097
90	0.1097	0.1096	0.1097	9.107	0.8965

TABLE V.—WHALE OIL.

30	0.3493	0.3477	0.3485	2.869	0.9192
50	0.1819	0.1824	0.1822	5.489	0.9063
70	0.1103	0.1099	0.1101	9.090	0.8912
90	0.07243	0.07238	0.07241	13.810	0.8782

TABLE VI.—MENHADEN-COD LIVER OIL MIXTURES.

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.
1 Per cent. Menhaden.				
30	0.3904	0.3900	0.3902	2.563
50	0.2006	0.2008	0.2007	4.983
70	0.1199	0.1198	0.1199	8.340
90	0.07878	0.07895	0.07887	12.680
25 Per cent. Menhaden.				
30	0.4284	0.4300	0.4292	2.330
50	0.2223	0.2223	0.2223	4.482
70	0.1295	0.1297	0.1296	7.716
90	0.08429	0.08429	0.08429	11.860
50 Per cent. Menhaden.				
30	0.4765	0.4760	0.4763	2.099
50	0.2394	0.2398	0.2392	4.181
70	0.1405	0.1405	0.1405	7.117
90	0.09118	0.09126	0.09122	10.960
75 Per cent. Menhaden.				
30	0.5331	0.5358	0.5344	1.871
50	0.2657	0.2646	0.2652	3.771
70	0.1535	0.1532	0.1534	6.519
90	0.09959	0.09943	0.09951	10.050

TABLE VII.—DOGFISH LIVER-COD LIVER OIL MIXTURES.

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.
1 Per cent. Dogfish.				
30	0.3893	0.3903	0.3898	2.569
50	0.2004	0.2005	0.2005	4.987
70	0.1188	0.1188	0.1188	8.417
90	0.07904	0.07879	0.07892	12.670
25 Per cent. Dogfish.				
30	0.3995	0.3996	0.3996	2.502
50	0.2037	0.2033	0.2035	4.914
70	0.1209	0.1211	0.1210	8.264
90	0.08000	0.08022	0.08011	12.480
50 Per cent. Dogfish.				
30	0.4075	0.4090	0.4082	2.450
50	0.2060	0.2059	0.2060	4.854
70	0.1249	0.1247	0.1248	8.013
90	0.08114	0.08132	0.08123	12.310
75 Per cent. Dogfish.				
30	0.4187	0.4203	0.4195	2.384
50	0.2099	0.2101	0.2100	4.762
70	0.1227	0.1224	0.1226	8.157
90	0.08146	0.08156	0.08151	12.270

TABLE VIII.—WHALE-COD LIVER OIL MIXTURES.

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.
1 Per cent. Whale.				
30	0.3883	0.3852	0.3868	2.585
50	0.1995	0.1994	0.1995	5.013
70	0.1189	0.1187	0.1188	8.417
90	0.07855	0.07845	0.07850	12.740
25 Per cent. Whale.				
30	0.3777	0.3777	0.3777	2.648
50	0.1944	0.1946	0.1945	5.141
70	0.1156	0.1157	0.1157	8.643
90	0.07754	0.07754	0.07754	12.000
50 Per cent. Whale.				
30	0.3686	0.3689	0.3688	2.711
50	0.1898	0.1894	0.1896	5.274
70	0.1134	0.1131	0.1133	8.827
90	0.07495	0.07491	0.07493	13.340
75 Per cent. Whale.				
30	0.3598	0.3596	0.3597	2.780
50	0.1863	0.1865	0.1864	5.365
70	0.1120	0.1115	0.1118	8.945
90	0.07480	0.07468	0.07474	13.380

The results are shown graphically in Figs. 1–5. In Figs. 1–4, fluidities of the oils are plotted as ordinates against composition of the mixtures as abscissas, the abscissas reading in percentages of cod oil; the four plots are taken from the fluidity readings at 30°, 50°, 70°, and 90°, respectively.

The fluidity curves are seen to be linear, and consequently it must be concluded that the fluidities of these oil mixtures are strictly additive over the range of temperature studied. According to what has been said, this confirms in a striking manner Bingham's fluidity hypothesis, which requires the above relationship between fluidity and composition in non-associated liquids. It has been indicated in a previous article[1] that these oils are slightly associated, the fluidity-temperature curve not being a straight line; but the deviation from a linear function is very slight and scarcely to be taken into consideration in this connection. Therefore, if the fluidity of a mixture of two oils is measured, and that of the constituents is known, the composition of the mixture may be calculated. It has been shown[2] that the viscosity of these oils is characteristic and fairly constant if the different samples of oil are obtained under similar conditions; fluidity data should then add to the knowledge desired, regarding the detection of adulteration in oils. Of course, taken alone, the fluidity would hardly be of great value in detecting any such adulteration, but when considered along with the results of other tests simultaneously applied, it furnishes additional evidence concerning the character of the oil studied.

The mixtures of one part of one oil to ninety-nine of the other were made up to test the accuracy and delicacy of the method. The introduction of this one per cent. of oil was readily detected by the viscosimeter used, and the fluidity of these mixtures was found to conform to the additive relationship.

Since the fluidities are found to be additive, the viscosity should be a hyperbolic function of the composition. The relation between the viscosity and the composition is shown graphically in Fig. 5, the temperature being 30°. The curve for the menhaden-cod mixtures deviates markedly from a straight line, that for the dogfish-cod mixtures less so, while the viscosity

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[1] THIS JOURNAL, 4, 109 (1912).

[2] *Ibid.*

of the whale-cod mixtures presents a linear function. The menhaden oil has a viscosity which varies from that of the cod to the greatest extent of any of the oils, and we should expect that curve to evidence the greatest curvature. These facts coincide with the following mathematical deduction of the relation between fluidity and composition suggested by Bingham.

Since the fluidity is a linear function of the composition, this may be expressed by the formula

$$\varphi = \varphi_1 + (\varphi_2 - \varphi_1)x \qquad (1)$$

where φ represents the fluidity of the mixture, φ_1 and φ_2 that of the two components, the latter being supposed to be the more fluid, and x the percentage of the latter in the mixture. The corresponding viscosity equation is

$$1/\eta = \varphi_1 + (\varphi_2 - \varphi_1)x,$$

where φ_1 and φ_2 are constants and η and x are variable, or

$$\eta = \frac{1}{\varphi_1 + (\varphi_2 - \varphi_1)x}. \qquad (2)$$

The curvature is therefore

$$\kappa = \frac{2(\varphi_2 - \varphi_1)^2[\varphi_1 + (\varphi_2 - \varphi_1)x]^3}{\{[\varphi_1 + (\varphi_2 - \varphi_1)x]^4 + (\varphi_2 - \varphi_1)^2\}^{\frac{3}{2}}}. \qquad (3)$$

By differentiating this curvature in respect to the concentration x, and equating to zero, we obtain the concentration where the curvature of the viscosity curve is a maximum to be

$$x = \frac{\sqrt{\varphi_2 - \varphi_1} - \varphi_1}{\varphi_2 - \varphi_1}. \qquad (4)$$

Substituting this value in equation (3), one obtains the amount of curvature where the curvature is a maximum to be

$$\kappa = \sqrt{\frac{\varphi_2 - \varphi_1}{2}}. \qquad (5)$$

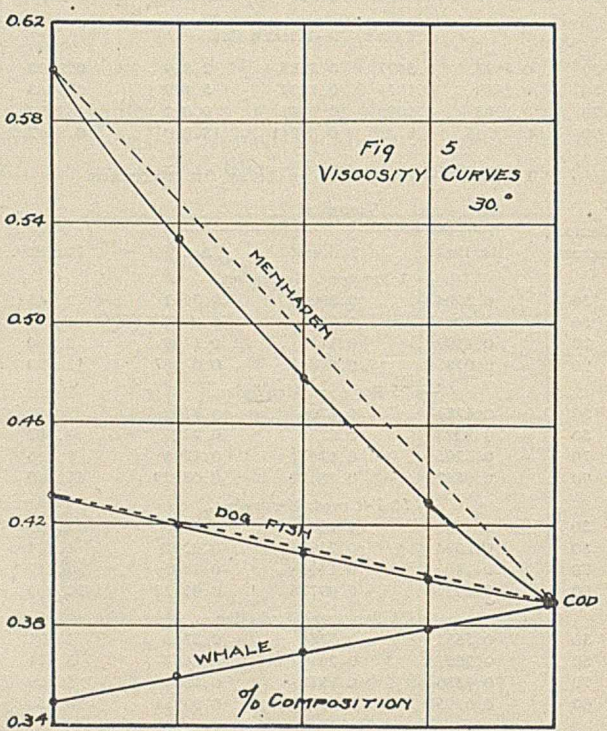
It follows, therefore, as a necessary consequence of the assumption that fluidities are additive that:

1. The curvature obtained by plotting viscosities is greatest when the difference between the fluidities, *i. e.*, $\varphi_2 - \varphi_1$, is large, and becomes zero when $\varphi_2 - \varphi_1 = 0$ [cp. equation (5)].

2. The curvature obtained by plotting viscosities must continually decrease as the concentration increases unless the square root of $\varphi_2 - \varphi_1$ is greater than φ_1, in which case the point of greatest curvature will be found at some positive concentration [cp. equation (4)].

3. Mathematically considered the curvature is dependent only upon the difference in the fluidities of the components, *i. e.*, $\varphi_2 - \varphi_1$ and not upon φ_1 [cp. equation (5)], but since we can only realize positive values of x, it follows that for a given value of $\varphi_2 - \varphi_1$ the curvature at any concentration will be greatest when φ_1 is very small.

That the curvature is greatest when the fluidities are quite unequal has already been noted by observers.[1] That the curvature is greatest when the viscosities are great has also been observed in the measurements of the viscosity of undercooled[1] and other very viscous liquids. It has caused some bewilderment, but we believe that the cause of this peculiarity has never before been given. The conclusion that the curvature is not uniform, is also clearly shown in the case of very viscous liquids. It is not shown very well by the curves which are given in this paper because the fluidities of the components are not sufficiently unequal.



In conclusion, it is possible that the fluidities and viscosities of oil mixtures *may* be simultaneously additive, but it seems to be a perfectly general rule that the fluidity is invariably a linear function of the composition so long as there is no marked action between the components.

I wish to express my gratitude to Dr. Eugene C. Bingham for valuable suggestions with regard to this investigation.

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COMPARATIVE VALUE OF IRRIGATED AND DRY-FARMING WHEAT FOR FLOUR PRODUCTION.

By ROBERT STEWART AND C. T. HIRST.

Received Nov. 10, 1911.

The Chemical Department of the Utah Experiment Station has been conducting investigations during the past eight years regarding the milling, chemical and baking characteristics of different varieties of wheat grown under irrigated and dry-farming conditions. A great many varieties of wheat have been

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[1] Thorpe and Rodger, *J. Chem. Soc.* (*London*), **71**, 361 (1896). Bingham, *Am. Chem. J.*, **35**, 195 (1906).

[1] Tammann, *Z. physik. Chem.*, **28**, 17 (1898).

investigated, many of which were imported from different sections of the country. The dry-farming varieties of wheat have been grown on the several experimental dry farms, while the irrigated varieties have been grown on the irrigated farm located in the Cache Valley at Greenville.

In 1908, a preliminary report of these investigations was published.[1] Some very important results were obtained. It was found that the dry-farming wheats were characterized by a low moisture and a high protein content. The fact that dry-farming wheats have a low moisture content is important. A difference of one per cent. in moisture in a large consignment of wheat renders the wheat having the lower moisture content of higher intrinsic value. It was found that the protein content of the flour produced from the durum varieties of wheat was 17.64 per cent. The protein content of the flour produced from the common bread varieties of wheat was found to be 16.79 per cent., while the protein content of the flour produced from irrigated wheat was found to be 13.34 per cent., thus clearly indicating the higher protein content of the flour produced from dry-farm wheats. It was found, however, that in many cases the millers were unable to produce good flour, from the baker's point of view, from the wheat they obtained from the farmers. These investigations showed that this was due to two causes: first, the most common variety of wheat grown in the state, the Gold Coin, contained the lowest protein content of any of the varieties of wheat tested; second, the farmers were not united on any one particular variety of wheat or any few varieties, but each farmer was governed in his choice of the variety by his own personal inclinations, irrespective of the quality of wheat grown. The work clearly demonstrated the necessity of uniting on one or two varieties of wheat to be grown by the farmers for bread-making purposes, and it also clearly demonstrated the necessity of uniting upon the variety of wheat having a high protein content, good chemical, milling and baking characteristics.

Since the publication of this bulletin, the work has been continued and the summarized results obtained by the three-year investigations, 1907–8–9, are given herewith.

The summarized results for the yield of milling products of spring and winter dry-farming and irrigated wheat during the years 1907–8–9 are recorded in Table I.

TABLE I.—SUMMARIZED RESULTS FOR YIELD OF MILLING PRODUCTS. RESULTS RECORDED AS PER CENT. OF DRY WEIGHT.

	Tests.	Weight 100 kernels.	Flour.	Bran.	Shorts.	Error.
Irrigated wheat, 25" water.....	10	4.008	68.08	23.39	8.52	—0.01
Irrigated wheat, 15" water.....	10	4.065	69.24	22.94	8.10	+0.28
No irrigation[2]...............	10	3.569	67.88	24.75	7.11	—0.26
Winter dry-farm wheat......	136	3.004	69.21	22.45	8.31	—0.03
Spring dry-farm wheat.......	17	3.106	66.09	20.95	12.13	—0.83

The weight per 100 kernels of the irrigated wheat is greater than that of either the spring or winter dry-farming wheat. The yield of flour, bran and shorts shows nothing characteristic for the wheats grown under different conditions.

The results obtained for the moisture content of the flour, wheat, shorts, and bran are brought together in Table II.

TABLE II.—SUMMARIZED RESULTS FOR MOISTURE IN FLOUR, WHEAT, SHORTS AND BRAN.

	Tests.	Flour.	Wheat.	Shorts.	Bran.
Irrigated wheat, 25 inches water....	10	10.41	8.46	9.41	8.54
Irrigated wheat, 15 inches water..	10	10.41	8.50	9.36	8.36
No irrigation..................	10	10.43	8.44	9.35	7.68
Winter dry-farm wheat..........	136	9.89	8.11	9.23	8.74
Spring dry-farm wheat...........	19	10.29	8.12	9.85	8.75

The moisture content is low in every case. The moisture content of the irrigated wheat is higher than that of the dry-farm wheat. The moisture content of the bran is practically the same as that of the wheat. The moisture content of the flour is about two per cent. higher than that of the wheat, while that of the shorts is about one per cent. higher than the wheat.

The results for the protein content of flour, wheat, shorts and bran are brought together in Table III.

TABLE III.—SUMMARIZED RESULTS FOR PROTEIN IN FLOUR, WHEAT, SHORTS AND BRAN.

	Tests.	Flour.	Wheat.	Shorts.	Bran.
Irrigated wheat, 25 inches water..	10	12.63	14.00	16.40	18.87
Irrigated wheat, 15 inches water..	10	12.92	14.35	16.89	18.66
No irrigation..................	10	13.62	15.45	17.67	19.32
Winter dry-farm wheat..........	136	14.64	15.76	18.27	20.87
Spring dry-farm wheat...........	19	15.74	16.85	19.17	20.39

It is thus seen that the lowest protein content is found in the irrigated wheat. This has been previously observed at this experiment station.[1] The result obtained for the same varieties of wheat grown on the same land but receiving no irrigation water clearly indicates that the decrease in protein is due to the influence of the water and not to differences in varieties grown on irrigated and dry-farming land. This difference is also observed in the flour, bran and shorts. It is manifest to a greater degree, however, in the flour when the yield is taken into consideration. The difference in the amount of water applied to the plots receiving 25" and 15" of water is not sufficient to make any marked difference in the amount of protein in the wheat, flour, bran and shorts, although a slight difference is noted. The difference between the protein content of wheat which had received 25 inches of irrigation water and the spring dry-farm wheat is 2.85, the difference in the protein content of the flour produced from these wheats 3.11, while that of the shorts and bran is 2.77 and 1.42 per cent., respectively.

The summarized results obtained for the chemical composition of the flour produced from spring, winter and irrigated grain are recorded in Table IV.

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[1] Stewart and Greaves, *Bull.* **103**, Utah Experiment Station.

[2] Wheat grown on *irrigated* land but receiving no irrigation water during the growing season; used as a check on application of varying amounts of water.

[1] Widtsoe, *Bull.* **80**, Utah Experiment Station.

TABLE IV.—SUMMARIZED RESULTS FOR CHEMICAL COMPOSITION OF FLOUR.

	Tests.	Moisture.	Protein.	Moist gluten.	Dry gluten.	Ratio of wet to dry gluten.	Ash.
Irrigated wheat, 25″ water.....	10	10.41	12.63	34.05	11.72	2.73:1	0.578
Irrigated wheat, 15″ water.....	10	10.41	12.92	32.55	11.63	2.79:1	0.544
No irrigation....	10	10.43	13.62	35.18	12.58	2.79:1	0.552
Winter dry-farm	136	9.89	14.64	40.14	14.14	2.85:1	0.529
Spring dry-farm	18	10.29	15.74	44.12	15.32	2.86:1	0.689

The flour produced from the winter dry-farm wheat has a slightly lower moisture content than the flour produced from the other kinds of wheat. The protein content of the flour produced from the wheat receiving the greatest amount of irrigation water is 3.11 per cent. lower than that produced from spring dry-farm wheat and 2.01 per cent. lower than that produced from dry-farm winter wheat. In case of the irrigated varieties of wheat, as the amount of water applied decreases, the protein content increases. The protein content of the flour produced from wheat which received no irrigation water is one per cent. greater than that produced from wheat receiving an application of 25 inches notwithstanding the fact that the seed wheat in both cases was the same and the non-irrigated wheat was grown on land which had been irrigated in previous years. The moist- and dry-gluten content of the flour produced from the irrigated wheat is considerably lower than that produced from either spring or winter dry-farm wheat.

The summarized results for the bread-making value of the flour produced from spring, winter dry-farm grains and the irrigated grains are recorded in Table V.

TABLE V.—SUMMARIZED RESULTS FOR BREAD-MAKING VALUE.

	No. of tests.	Cc. of water added.	Cc. of water retained.	Ratio of protein to vol. of water added.	Wt. of loaf.	Vol. of loaf.	Ratio of protein to vol. of loaf.
Irrigated wheat, 25″ water......	10	204	104	1:16.4	474	1605	1:127.1
Irrigated wheat, 15″ water......	10	185	105	1:14.3	475	1630	1:126.2
No irrigation......	10	204	109	1:15.1	479	1655	1:121.5
Winter dry-farm.	108	195	104	1:13.3	474	1681	1:114.8
Spring dry-farm...	11	227	124	1:14.4	494	1841	1:117.0

The ratio of protein to volume of water added is narrower in case of the dry-farm grains. The volume of loaf made from dry-farm flour is slightly greater than that produced from irrigated flour. The ratio of protein to volume of loaf is narrower in the dry-farm flour than in the irrigated flour.

The investigations extending over a period of eight years clearly demonstrate the fact that the dry-farm grains in Utah are characterized by a low moisture content and a high protein content. They also clearly indicate that the protein content of the dry-farm wheats is higher than the protein content of the wheat on irrigated farms.

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THE INFLUENCE OF CARBON UPON NITRIFICATION.

By H. W. CLARK AND GEORGE O. ADAMS.

Received November 24, 1911.

During the past twenty-three years many experiments have been made at the Lawrence Experiment Station of the Massachusetts State Board of Health to determine the effect upon nitrification of an excess of a number of substances which may occur naturally in sewage or may at times find their way into it. The substances previously studied—the results in regard to which have been given in the various reports of the Station and especially in that of 1908—have been albumen, peptone, ammonium chloride and sodium carbonate, sulfuric acid, saltpeter, common salt, sugar, soap, urine, free oxygen, phenol, mercuric chloride, formalin, arsenic, naphthalene, sulfides, bleaching powder and copper sulfate. As stated in the conclusions of the summary of this work in the report of 1908, "the experiments illustrate the adaptability of the nitrifying body to the conditions imposed and establish another fundamental law of sewage purification that if nitrification is to continue in the presence of an excess of any substance, the filter must become slowly accustomed to the presence of that substance by application of it in gradually increasing amounts; that when once accustomed to considerable amounts of any substance, the process of nitrification will proceed unimpaired." It, of course, follows, however, that a great excess of any substance inimical to nitrification will prevent nitrification.

In the various investigations necessitated by the work of the State Board of Health, many experiments have been carried on in regard to the purification of mill wastes by filtration, many of these wastes containing large amounts of carbonaceous and small amounts of nitrogenous matter. It appeared from this work that at times with many of these wastes and at all times with some of them, good purification and a satisfactory effluent could be obtained when nitrates were not found in the effluents of the filters operated. Studies of this phenomenon appeared to show that whether nitrification occurred or not depended upon the relation of the amount of carbonaceous to nitrogenous matter present in the liquid or waste undergoing treatment; that is to say, nitrification could apparently proceed when the amount of nitrogen was represented by x and carbon by $10x$ but would be eliminated when the carbon was increased to 12 or $15x$. In order to make a thorough investigation of this subject, certain experimental filters were put into operation early in the year 1910 and the work has continued until the present time (September, 1911). The method has been to apply to the sand filters used, Lawrence sewage freed from matter in suspension to which has been added some body rich in carbon. Practically all the carbon and nitrogen applied has been in solution and by this means surface clogging and storage of organic matter in the filters has been prevented.

The bodies added to the different filters with the sewage, have been sugar, molasses, butyric acid, alcohol and filtered wool-scouring waste, and these filters have been operated generally at a rate of 50,000 gallons per acre daily. Careful and frequent determinations of the relation between the carbon and the nitrogen in the liquid applied have been made and also frequent analyses of the effluent from each filter. The carbon values were calculated in the case of sugar, alcohol and butyric acid, the composition of which was known, and in the case of molasses the approximate composition of which could be calculated. The carbon content of the sewage used and of the filtered wool-scourings were calculated from data obtained from other experiments upon the relation between loss on ignition and carbon.[1] While it is not feasible to present in this article the full data in regard to this investigation, the data in regard to the operation of several filters are given beyond to show the general method followed and the results obtained. In all, twenty filters have been operated.

In the operation of the filters the carbon-containing bodies have generally been added in slowly increasing amounts, while the nitrogen applied has been kept constant. During the period when the ratio of carbon to nitrogen has remained low, active nitrification has occurred in each filter and high nitrates have been present in their effluents. When nitrification has been checked by the large amounts of carbon applied, each filter has been continued in operation long enough to prove conclusively that nitrification would not again become active until the ratio of carbon to nitrogen was considerably reduced and also long enough to prove that good purification continued without nitrifying conditions in the filter. In all instances several duplicate experiments with the same carbonaceous substance were made in order to prevent errors in our work and conclusions. Experiments were also made showing that when nitrification had been checked, but not entirely stopped by the carbon, it would be re-established by increasing the amount of nitrogen in the liquid applied and keeping the carbon constant, this, of course, reducing the ratio of carbon to nitrogen. It was also found that when ammonium chloride was added to the sewage, nitrification was not checked by carbonaceous bodies even when added in very large amounts.

The main results of these experiments can be summarized as follows:

When sugar was added in such amounts that the applied liquid contained less than 50 parts of carbon, nitrification was stopped in three separate experiments when the average carbon to nitrogen ratio was 13, 14 and 15. When the ratio was 11.6, 11.1 and 11.0, nitrification was not seriously checked. When nitrogen as NH_4Cl was added, nitrification took place even when 200 parts of carbon as sugar was present in the applied liquid, and the ratio of carbon to nitrogen was 10.8. When molasses was added with the sewage, nitrification was stopped when the average carbon to nitrogen ratio was above 12, but active when this ratio was 10 and 11. With butyric acid, nitrification was not seriously impeded when the average carbon to nitrogen ratio varied between 13 and 16, but was prevented when the carbon to nitrogen ratio was 27. When nitrogen as NH_4Cl was added with the butyric acid, nitrification took place even when acid equivalent to 200 parts carbon was present, the ratio of carbon to nitrogen being 14.0. With alcohol, nitrification was active when the average carbon to nitrogen ratio was 13 and 13.8, but was stopped when the average ratio was 15 and 16. When nitrogen as NH_4Cl was added with the alcohol, 400 parts of alcohol equal to 160 parts carbon could be applied to the filter and nitrification remain active, the carbon to nitrogen ratio under these conditions being 12.2. With filtered wool-scouring waste diluted with water, nitrification continued as long as the carbon to nitrogen ratio was below 14, the carbon running up to 350 parts per 100,000 but was stopped when the carbon to nitrogen ratio was increased to 17 by the addition of sugar.

Data in regard to three of these filters follow, and it will be noticed that even when nitrification ceased and the filters continued in operation, the amount of free and albuminoid ammonia present in the effluents of these filters was little, if any, greater than when nitrification was active. This occurred although the same amount of nitrogenous matter was being applied as when nitrification was active.

As stated in the beginning of this article, these results are similar to those obtained frequently with mill wastes and occasionally with domestic sewage and show that purification can take place in certain filters under the conditions imposed by the addition of large amounts of carbonaceous matter even although nitrification in the filter ceases. This purification without nitrification is due to certain bacteria which are active under conditions which prevent nitrification but cause chemical actions which break down organic matter and result in the setting free of carbon dioxide and nitrogen. It is distinctly different from the action sometimes occurring in contact filters where the nitrates formed do not appear in the effluent, as in such filters further oxidation of organic matter is accomplished within the filter by the use of the oxygen of these nitrates and their consequent reduction. The intense activity of the filter in changing

FILTER RECEIVING SEWAGE TO WHICH MOLASSES WAS ADDED. ANALYSES AT INTERVALS.

(Parts per 100,000.)

Free ammonia:					
Applied liquid	4.30	2.28	3.03	2.25	2.40
Effluent from filter	0.188	0.14	0.15	0.27	0.27
Albuminoid ammonia:					
Applied liquid	0.33	0.31	0.39	0.39	0.42
Effluent from filter	0.026	0.036	0.04	0.042	0.046
Oxygen consumed:					
Applied liquid	12.14	16.99	19.10	23.80	23.80
Effluent from filter	0.22	0.26	0.35	0.31	0.39
Kjeldahl nitrogen:					
Applied liquid	0.67	0.76	0.76	0.85	0.84
Nitrogen as nitrites:					
Effluent from filter	0.0016	0.0014	0.0012	0.0004	0.0002
Nitrogen as nitrates:					
Effluent from filter	2.52	2.18	2.01	0.84	0.10
Total carbon:					
Applied liquid	34.8	50.4	55.5	68.5	68.5
Ratio C/N:					
Applied liquid	8.3	16.1	17.0	24.4	24.3
Per cent. applied nitrogen in effluent	65.0	75.0	68.0	39.0	15.0

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[1] THIS JOURNAL, 3, 738.

carbonaceous matter to the gaseous form, and its liberation and disappearance in this way, is strikingly shown by the oxygen-consumed results of the applied liquid and effluent. The loss of nitrogen by its liberation can be seen by the figures showing the percentage of that applied appearing in each effluent during different periods of operation of each filter.

FILTER RECEIVING SEWAGE TO WHICH BUTYRIC ACID WAS ADDED. ANALYSES AT INTERVALS.

(Parts per 100,000).

Free ammonia:							
Applied liquid....	3.03	3.03	2.70	2.98	2.98	2.98	2.98
Effluent from filter	0.22	0.12	0.18	0.088	0.17	0.148	0.13
Albuminoid ammonia:							
Applied liquid....	0.25	0.25	0.20	0.25	0.27	0.27	0.27
Effluent from filter	0.028	0.02	0.014	0.036	0.036	0.038	0.044
Oxygen consumed:							
Applied liquid....	2.69	2.69	2.00	2.00	2.00	2.00	2.00
Effluent from filter	0.21	0.23	0.22	0.26	0.18	0.22	0.21
Kjeldahl nitrogen:							
Applied liquid....	0.64	0.64	0.50	0.64	0.65	0.65	0.65
Nitrogen as nitrites:							
Effluent from filter	0.004	0.002	0.0012	0.0006	0.0006	0.0006	0.0006
Nitrogen as nitrites:							
Effluent from filter	0.75	0.63	1.01	2.40	0.34	0.05	0.05
Total carbon:							
Applied liquid...	37.6	37.6	37.6	54.0	84.7	84.7	84.7
Ratio C/N:							
Applied liquid...	12.0	12.0	13.8	17.5	27.4	27.4	27.4
Per cent. applied nitrogen in effluent	32.0	25.0	44.0	82.0	18.0	8.0	8.0

FILTER RECEIVING SEWAGE TO WHICH SUGAR WAS ADDED. ANALYSES AT INTERVALS.

(Parts per 100,000).

Free ammonia:							
Applied liquid....	3.30	3.82	3.84	2.88	3.03	2.25	2.40
Effluent from filter	0.02	0.022	0.024	0.018	0.034	0.05	0.14
Albuminoid ammonia:							
Applied liquid....	0.25	0.24	0.27	0.21	0.19	0.19	0.17
Effluent from filter	0.02	0.012	0.016	0.026	0.02	0.022	0.022
Oxygen consumed:							
Applied liquid....	1.60	14.22	13.40	13.50	15.50	13.90	14.00
Effluent from filter	0.13	0.12	0.18	0.16	0.18	0.14	0.15
Kjeldahl nitrogen:							
Applied liquid....	0.47	0.56	0.45	0.76	0.36	0.45	0.34
Nitrogen as nitrites:							
Effluent from filter	0.0040	0.0012	0.0004	0.0004	0.0004	0.0002	0.0002
Nitrogen as nitrates:							
Effluent from filter	3.11	1.39	2.65	2.86	1.43	0.67	0.04
Total carbon:							
Applied liquid....	4.7	40.7	39.2	41.6	45.5	46.0	43.3
Ratio C/N:							
Applied liquid....	1.5	11.0	10.9	14.7	15.9	20.0	18.4
Per cent. applied nitrogen in effluent	99.1	38.5	74.7	104.0	52.0	33.0	9.0

MILL WASTE FILTERS.

The following table shows the average results obtained during the past fifteen years of a number of filters operated with various mill wastes. The effluents from all these filters have been stable and usually clear and odorless. It will be noticed that where the ratio of carbon to nitrogen in the waste applied to the filter is around 10, there has been nitrification. In the case of the carpet mill waste, the first filter gave no nitrification because the carbon to nitrogen ratio was 16.1. This filter reduced the carbon to nitrogen ratio of the liquid to 9.0 so that when applied to a second filter, nitrification took place in the secondary filter.

	Applied waste. (Parts per 100,000.)			Effluent. (Parts per 100,000.)
Waste from:	Total Nitrogen.	Approximate amount of carbon.	Ratio C/N.	Nitrogen as nitrates.
Dyeing cotton	0.58	41.6	71.0	0.02
Washing and dyeing cotton	0.76	21.8	28.6	0.01
Dyeing and finishing	0.57	11.4	20.0	0.00
Dyeing and finishing	0.27	5.2	19.2	0.07
Cotton batting	1.25	21.9	17.5	0.04
Carpet mill	2.24	3.6	16.1	0.05
Dyeing and finishing	1.80	26.8	14.9	0.10
Scouring and dyeing	0.91	10.8	11.9	0.37
Effluent from carpet mill filter No. 2	0.93	8.5	8.9	0.32
Binders' board	0.49	4.0	8.1	0.11
Shoddy mill	0.77	4.0	5.2	1.01
Tannery	4.65	19.4	4.0	3.63

LAWRENCE EXPERIMENT STATION,
MASS. BOARD OF HEALTH.

ACIDITY IN WHEAT FLOUR; ITS RELATION TO PHOSPHORUS AND TO OTHER CONSTITUENTS.

By C. O. SWANSON.

Received Jan. 25, 1912.

The investigation of the relation between chemical composition and the baking qualities of wheat flour is one of the major lines of investigation followed by the Chemical Department of the Kansas State Agricultural College Experiment Station. The chemical work in connection with this paper was done by Mr. John W. Calvin, Assistant Chemist, and Miss Leila Dunton, Fellow in Chemistry.

In our work on commercial flours it was noticed that there was an unmistakable relation between the percentages of acidity and the percentages of ash, amino compounds, total and water-soluble phosphorus. It was also noted that the acidity value and the related compounds depended to a large extent upon the method of milling. The presence of varying amounts of bran fiber or germ was more pronounced than any other factor.

To eliminate these factors of unknown influence it was decided to work on flours from different mill streams. The advantage of such flours was that their origin in relation to the different portions of the wheat kernel was better known. Also such flours would differ from each other to such an extent that small variations in the results due to experimental error would have less influence. In fact the differences on most of such flours are so great that the experimental error can in no way influence the main results. The description of the flours is given below. The wheat from which all these flours were made is also included. The serial numbers are the ones used throughout the discussion:

SERIAL NO.	DESCRIPTION OF SAMPLE, GIVING SOURCE.
389	Wheat from which the following twenty-six flours were made.
390	Patent flour, seventy per cent.
391	Clear flour, twenty-seven per cent.
392	Low-grade flour, three per cent.
393	First break flour, part of the clear.
394	Second break flour, part of the clear.
395	Third break flour, part of the clear.
396	Fourth break flour, part of the clear.
397	Fifth break flour, part of the clear.
398	First middlings flour, part of the patent.
399	Second middlings flour, part of the patent.
400	Third middlings flour, part of the patent.
401	Fourth middlings flour, part of the patent.

402	Fifth middlings flour, part of the patent.
403	Sixth middlings flour, part of the clear.
404	Seventh middlings flour, part of the clear.
405	First sizings flour, part of the patent.
406	Chunks flour, part of the patent.
407	Second sizings flour, part of the clear.
408	B middlings flour, part of the clear.
409	First tailings flour, part of the clear.
410	Second tailings flour, part of the clear.
411	Second low-grade flour, part of the low-grade.
412	Bran duster flour, part of the low-grade.
413	Ship duster flour, part of the low-grade.
414	Roll suction stock, part of the low-grade.
415	Stock going to fourth middlings from second sizings.

The chemical analyses of these flours for ash, protein, fat, acidity at 25° C. and 40° C., amino compounds, water-soluble phosphorus at 25° C. and 40° C. and total phosphorus are given in the accompanying table. The ash was determined by the calcium acetate method. The acidity was determined under two conditions: (1) the usual method, one-half hour extraction (room temperature about 25° C.) and (2) two hours' extraction at 40° C. That this latter method gives the maximum acidity was determined in a separate trial. The extracts from the acidity determinations were used in the determination of soluble phosphorus. The amino compounds were determined as follows: Eleven grams of flour were placed in a 600 cc. Erlenmeyer flask and 400 cc. of a 1% solution of sodium chloride added. The whole was thoroughly shaken and the shaking repeated every ten minutes for one hour. It was then allowed to settle for thirty minutes when a little over 200 cc. were filtered off. To exactly 200 cc. of the filtrate were added 20 cc. of a 10% solution of phosphotungstic acid. This was allowed to stand over night and then filtered. This filtrate was perfectly clear: 200 cc. of the filtrate were placed in a Kjeldahl flask, 5 cc. of sulphuric acid added, placed over a burner and the solution evaporated to 25 cc. More sulphuric acid was then added and the nitrogen determination finished in the regular way. The amino compounds were calculated as proteins. The percentage of the total phosphorus which is water-soluble was calculated and these figures are given in the last column.

ASH CONTENT.

The ash percentage increases in almost the same proportion as the flour contains fibrous branny material, or as the flours are taken from the portion of the wheat kernel next to the bran. The fifth break flour is highest in ash percentage, and the first break flour is next. The relatively high ash percentages of the first break flour is due to the incorporation of bran fibers when the flour is made, but in the fifth break the high ash content results from two causes: (1) the incorporation of bran fiber as in the first break and (2) the material in the wheat kernel next to the bran contains nore mineral matter than the interior of the kernel. This assumption is based on the composition of these mill streams in general. The middlings flours are lowest in ash. These are made from the interior portion of the kernel and by means of the purifiers they are very carefully freed from bran fibers. The flour from the chunks has a higher ash percentage than any of the streams which go into the patent flour. These chunks contain a relatively large amount of bran fiber and in grinding some of these fibers get into the flour. The ash content of bran and shorts is ten times that of flour. The percentage of ash furnishes a very good indication of the quality of the flour as far as that is related to the method of milling.

ACIDITY.

The acidity values, at 40°, two hours' extraction, show very clearly what portion of the wheat kernel the flour comes from.

As all these flours were made from the same wheat the effect of the unsound grain is eliminated. The presence of bran fiber, germ, or portions of the wheat kernel next to the bran, will largely influence the acidity values, probably more than unsoundness.

AMINO COMPOUNDS.

The amino compounds vary almost identically as the acidity and the same factors which influence the acidity also influence the percentage of amino compounds.

PHOSPHORUS.

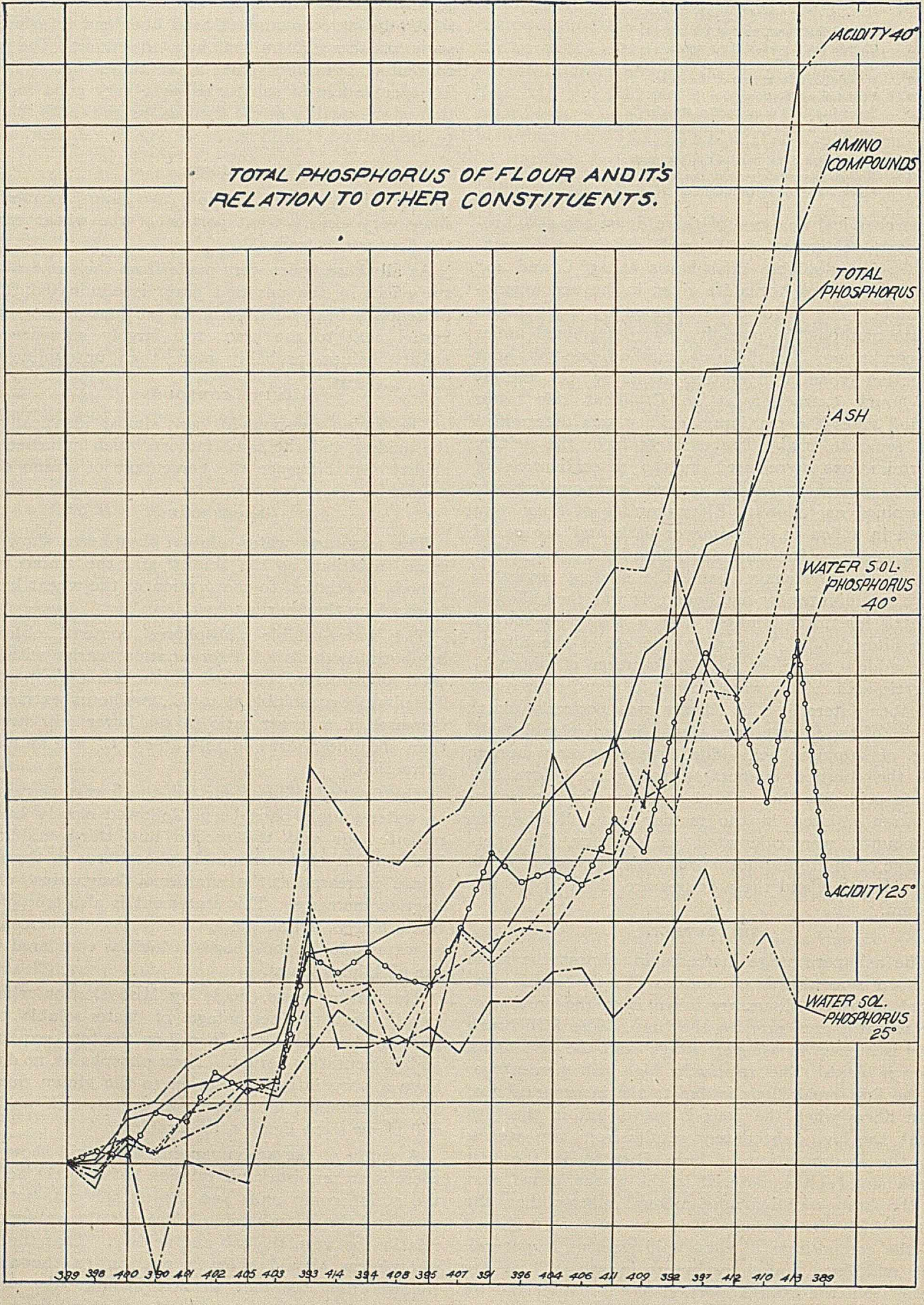
The total and water-soluble phosphorus show the same variations as the acidity and the amino compounds in relation to the portion of the wheat kernel from which the flour is taken.

The water-soluble phosphorus content, obtained by both methods of determination, varies with the total phosphorus, but not in the same proportion. The phosphorus soluble at 40° C., two hours' extraction, increases in a larger ratio in the lower mill streams than the phosphorus soluble at 25° C., half an hour's extraction.

The first middlings flour has the lowest percentage of water-soluble phosphorus followed closely by the patent flour and the second and third middlings. The amount of water-soluble phosphorus in the middlings increases as the number of designations of reduction increases. This statement is also true of the break flours. In all the lower streams, the percentage of water-soluble phosphorus is high as compared with the middlings flours.

The baking tests, made by Miss Dunton, showed clearly that the percentage of water-soluble phosphorus has a distinct influence on the total expansion and fermentation period. These phosphates, no doubt, have a very intimate relation to the gluten quality, and experiments are now in progress which we hope will throw some light on the problem.

A study of the accompanying table will show that there is an unmistakable relation between the acidity, the amino compounds and the phosphorus, both the total and the water-soluble. There is also an apparent relation between the ash and acidity. That the total phosphorus should show a relation to the acidity follows from the fact that it includes the soluble phosphates and the total and the soluble bear a more or less definite relation to each other. The larger



TOTAL PHOSPHORUS OF FLOUR AND IT'S RELATION TO OTHER CONSTITUENTS.

part of the phosphorus in the flour extract is probably in the form of phosphates of potassium. There are also smaller amounts of the phosphates of magnesium and calcium, the former being about four times as abundant as the latter, reasoning from the composition of wheat ash. The acid phosphates of magnesium are very slightly soluble in water. While monocalcium phosphate is soluble in water, the possible amount of this salt in the flour is very small. Reasoning from the different amount of inorganic elements present in the flour, much the larger part of the soluble phosphorus obtained in the extract is in the form of the phosphates of potassium. All the phosphates of potassium are more or less soluble in water. Some are soluble in alcohol while others are not. Orthopotassium phosphate is slightly soluble in cold water and the solubility increases at a higher temperature. Monopotassium phosphate and dipotassium phosphate are both soluble in cold water; the former gives a solution acid in reaction, while the latter gives a solution alkaline in reaction. It thus becomes evident why a soluble phosphate obtained from a flour will influence the acidity test. The effect of varying temperature on solubility of the different phosphates of potassium partly explains why the percentages are higher at 40° C.

Chemical Composition of Flour from Different Mill Streams. Moisture-Free Percentages.

No.	Mill stream.	Ash.	Acidity.		Amino comp.	Phosphorus.			
			25°.	40°.		Water sol. at 25°.	Water sol. at 40°.	Total.	Per cent. of water soluble at 40°.
389	Wheat	1.93	0.156	0.478	0.530	0.066	0.218	0.482	51.73
390	Patent 70 per cent.	0.52	0.074	0.130	0.162	0.021	0.028	0.110	29.25
391	Clear 27–27 ½ per cent.	0.83	0.170	0.245	0.270	0.071	0.098	0.187	59.64
392	Low grade 2 ½–3 per cent.	1.08	0.215	0.339	0.396	0.097	0.152	0.269	64.01
393	First break	0.93	0.136	0.239	0.276	0.053	0.082	0.162	57.79
394	Second break	0.80	0.137	0.211	0.239	0.060	0.083	0.165	57.45
395	Third break	0.80	0.126	0.220	0.237	0.062	0.084	0.172	55.74
396	Fourth break	0.88	0.160	0.252	0.266	0.071	0.103	0.204	78.34
397	Fifth break	1.28	0.235	0.370	0.363	0.114	0.187	0.296	72.29
398	First middlings	0.52	0.071	0.101	0.195	0.017	0.023	0.094	27.43
399	Second middlings	0.50	0.067	0.109	0.200	0.017	0.025	0.093	30.55
400	Third middlings	0.54	0.069	0.125	0.206	0.026	0.033	0.107	34.93
401	Fourth middlings	0.58	0.081	0.142	0.201	0.026	0.042	0.118	40.26
402	Fifth middlings	0.62	0.067	0.148	0.217	0.031	0.044	0.120	41.58
403	Sixth middlings	0.62	0.094	0.164	0.229	0.039	0.053	0.133	44.89
404	Seventh middlings	0.95	0.164	0.275	0.335	0.080	0.102	0.215	53.69
405	First sizings	0.64	0.091	0.161	0.194	0.042	0.051	0.127	46.21
406	Chunks	1.02	0.159	0.289	0.312	0.082	0.118	0.225	59.74
407	Second sizings	0.88	0.145	0.236	0.278	0.054	0.091	0.186	56.02
408	B. middlings	0.72	0.129	0.208	0.243	0.057	0.077	0.171	25.47
409	First tailings	1.15	0.170	0.304	0.317	0.076	0.145	0.261	63.16
410	Second tailings	1.36	0.186	0.395	0.444	0.094	0.175	0.327	60.68
411	Second low grade	1.01	0.181	0.305	0.340	0.065	0.122	0.230	59.51
412	Bran duster flour	1.27	0.220	0.370	0.404	0.080	0.161	0.301	59.91
413	Ship duster flour	1.58	0.239	0.466	0.505	0.070	0.191	0.373	57.53
414	Roll suction stock	0.79	0.130	0.467	0.239	0.068	0.078	0.164	53.72
415	Middlings from second sizings	0.46	0.065	0.133	0.076	0.023	0.079	0.113	79.20

Whether or not these phosphates are present as such in the flour or produced by the hydrolytic action of the water in the process of extraction is immaterial as far as they influence the acidity value. It is this water extract that is used for the determination of acidity, and in which the acid phosphates would be found. It may be that the greater part of the phosphorus in the flour is present in the organic form. Determinations made in this laboratory seem to point that way, but the hydrolytic action of the water during extraction may easily change this condition.

In the following discussion, the figures for 70 per cent. patent flour, treatment at 40° C. two hours, are taken. The percentage acidity is 0.130. This corresponds to 2.88 cc. $N/20$, or 0.0081 g. KOH for 10 g. of flour. The per cent. of water-soluble phosphorus in an extract from the same amount of flour and obtained under the same condition is 0.028. This would correspond to 0.0028 g. of phosphorus; that is, the water extract which requires 0.0081 g. of KOH to neutralize the acidity contains 0.0028 g. of soluble phosphorus in the form of acid phosphates. Assuming that this phosphorus is in the form of monopotassium phosphate, there would be 0.0123 g. of this salt.

Assuming the chemical reaction to take place in accordance with the following equation,

$$KOH + KH_2PO_4 = K_2HPO_4 + H_2O,$$

we have the following proportion:

$$56.1 : 136.1 : : 0.0081 : X = 0.0196$$

This means that it would take 0.0196 g. of monopotassium phosphate to be neutralized by the 0.0081 g. of KOH, while according to the determinations there was only 0.0123 g. of this salt present as calculated from the amount of soluble phosphorus. If we assume the above reaction to take place this amount of monopotassium phosphate would require only 0.0051 gram of KOH for its neutralization. The difference between 0.0081 and 0.0051 or 0.003 g. of KOH would be neutralized by some other compounds. That these compounds are the amino acids is evident from the close relation between the acidity value and the amino compounds. The close relation between the ash percentages and the acidity is due to the greater content of phosphorus in the samples which are high in ash.

GRAPHIC PRESENTATION OF THE RELATION BETWEEN PHOSPHORUS AND OTHER CONSTITUENTS IN MILLSTREAM FLOURS.

The figures for total phosphorus given in the table of analyses were arranged in an ascending series and the figures for the other constituents placed in parallel columns. These figures were then plotted on cross-section paper with the results shown in the accompanying plate. To bring the curves near each other on the plate, the figures for each constituent of No. 399, second middling flour, were reduced by addition and subtraction to the same value as the figure for total phosphorus. The corresponding figures for the constituents of all the flours were treated by the same factors as were used in changing the numerical values for the constituents on No. 399. This does not change the form of the curve but the relative position is changed. Unless some such method were used, it would not be possible to show all these curves on one plate. But, it should be borne in mind that on account of these calculations, the fact that one curve is above another does not mean that the absolute value is greater. The plate shows only the relation of the curves to each other, not the relative magnitude of the constituents represented.

THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

By Charles Baskerville and W. A. Hamor.

Received December 13, 1911.

(Continued from the March No.)

V. The Physical Constants of Chloroform.

1. SPECIFIC GRAVITY.

A. The earliest determinations of the density of chloroform were made in 1832 by Liebig,[1] who reported the constant 1.485 at 15°, and by Guthrie,[2] who found the value to be 1.486 at 15.5°. Later (1849), Soubeiran and Mialhe[3] obtained a purer preparation, as shown by their density determination, 1.4905 at 15°. Up to 1849, however, the best commercial chloroform possessed a specific gravity of 1.480, which was considered a guarantee of its purity. Gregory[4] found that chloroform of the density 1.480, when once treated with sulphuric acid, which destroyed the "oils," might be obtained, after removing the "sulphurous acid," of the density of 1.500 at 15.5°. This value he took as the true specific gravity of chloroform. Wilson was unable to obtain chloroform of a density higher than 1.498; but Gregory considered his chloroform impure, and stated that every sample, whether originally of 1.480, 1.490, or 1.497, when purified by means of sulphuric acid and manganese dioxide, acquired the density which he regarded as true, *viz.*, 1.500 at 15.5°.

Schiff,[1] in 1858, reported that chloroform possesses a density of 1.5066 at 15°; this high result was probably attributable to the method of purification which he employed. In 1865, Hager stated that "pure" chloroform possesses a density of 1.494–1.495 at 15°.[2] Swan[3] reported that his determinations showed 1.493–1.497; but these results, like those of Soubeiran and Mialhe, and Gregory, were due to the fact than no special pains were taken to free the chloroform from alcohol.

The determinations of Thorpe[4] were made on chloroform which had been carefully purified,[5] and undoubtedly represent great accuracy. Thorpe found the density to be 1.52657 at 0°/4°, with which value the recent determinations of Timmermans,[6] 1.52633–7 for d_4°, are in accord. A summarization of the various determinations of the specific gravity of chloroform is given in Table I.

Table I.—Various Determinations of the Specific Gravity of Chloroform.

0°.	11.8°.	12°.	15°.	15.5°.	16.5°.	17°.	18°.
1.52523[7]	1.5039[9]	1.496[10]	1.485[12]	1.500[23]	1.472[24]	1.491[25]	1.48[27]
1.52657[8]		1.512[11]	1.4946[13]			1.507[26]	
			1.4905[14]				
			1.4976[15]				
			1.5066[16]				
			1.5107[17]				
			1.4989[18]				
			1.4980[19]				
			1.500[20]				
			1.50027[21]				
			1.50085[22]				

18.58°.	25°.	29°.	35.86°.	60.8°.	61.2°.	63°.
1.48978[28]	1.48432[29]	1.49089[30]	1.45695[31]	1.4081[32]	1.40877[33]	1.3954[34]
	1.48492[29]					1.4018[35]
						1.40814[36]

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[1] *Ann.*, **1**, 199.

[2] *Am. J. Sci.*, [1] **22**, 105.

[3] *Jahresber.*, **2**, 408. The densities given were calculated from the values reported.

[4] *Pharm. J.*, **9**, 580.

[1] *Ann.*, **107**, 63.

[2] *Kommentar*, **439.** The requirement of the *Pharmacopoea Borussica* at this time was 1.492–1.496. "English Chloroform," already referred to, possessed a density of 1.485.

[3] *Phil. Mag.*, [3] **33**, 38.

[4] *Trans. Chem. Soc.*, **37**, 196.

[5] The method employed has already been described under *Purification*.

[6] *Bull. soc. belg. chim.*, **24**, 244.

[7] Pierre, *Compt. rend.*, **27**, 213.

[8] Thorpe, *J. Chem. Soc.*, **37**, 371. Referred to water at 4°.

[9] Schiff, *Gazz. chim. ital.*, **13**, 177. Water at 4°.

[10] Soubeiran and Mialhe, *Jahresber.*, **2**, 408. Not free from alcohol

[11] Schiff, *Ann.*, **107**, 63.

[12] Calculated from [21].

[13] Calculated from [19].

[14] Calculated from [4].

[15] Calculated from [1].

[16] Calculated from [5].

[17] Calculated from [20].

[18] Calculated from [2].

[19] Calculated from [3].

[20] Remys, *J. Chem. Soc.*, **13**, 439.

[21] Perkin, *J. prakt. Chem.*, [2] **32**, 523. Water at 15°.

[22] Perkin, *Ibid.* Water at 15°

[23] Gregory, *Jahresber.*, **3**, 454. Not free from alcohol.

[24] Geuther.

[25] Regnault, *Ann. chim. phys.*, [2] **71**, 381.

[26] Flückiger, *Z. anal. Chem.*, **5**, 302. Water at 17°.

[27] Liebig, *Ann.*, **1**, 199.

[28] Drecker, *Pogg. Ann.*, [2] **20**, 870.

[29] Perkin, *Loc. cit.* Water at 25°.

[30] Nasini, *Gazz. chim. ital.*, **13**, 135.

[31] Drecker, *Loc. cit.*

[32] Schiff, *Ber.*, **15**, 2972.

[33] Thorpe, *Loc. cit.*

[34] Ramsay, *J. Chem. Soc.*, **35**, 463.

[35] Schiff, *Ber.*, **14**, 2763.

[36] Schiff, *Ibid.*

In the course of their investigation of the decomposition of chloroform, the authors had occasion to prepare chloroform which they regard as absolutely pure.[1] This possessed a density of 1.49887 at 15°/4° (average of six determinations), a result in close agreement with the values of Thorpe and Timmermans, and which we consider to be the correct specific gravity at this temperature.

B. The anaesthetic chloroform on the American market varies in specific gravity from 1.4730–1.4827 at 25°/25°, usually in close proximity to 1.476, the minimum density permitted by the *Pharmacopoeia*. The samples of chloroform of German manufacture examined by the authors varied in specific gravity from 1.487–1.492 at 15°/15°, although one sample possessed a density of 1.497 at this temperature. Since the correct specific gravity of chloroform is 1.49887 at 15°/4° those authorities requiring chloroform of a lower density—that is, anaesthetic chloroform—allow the addition of alcohol, and consequently the presence of small amounts of water; the permissible addition usually varies from 0.5–1 per cent.[2]

The specific gravities of the chloroforms recognized as official by the pharmacopoeias of various countries are given in Table II.[3]

TABLE II.—DENSITIES ACCORDING TO VARIOUS PHARMACOPOEIAS.

1.480	1.489	1.490	1.497	1.498	1.500	1.485–1.489	1.485–1.490
Spain[4] Portugal[5] Mexico[6]	Switzerland[7]	Greece[8]	Chili[9]	France[10]	Roumania[11]	Germany[12] Denmark[13] Hungary[14] Norway[15] Sweden[16] Finland[17]	Belgium[18]

1.485–1.495	1.485–1.500	1.490–1.493	1.490–1.495	1.498–1.500	1.499–1.500	Not below 1.476 at 25°
Japan[19]	Austria[20]	Italy[21]	Great Britain[22]	Holland[23]	Russia[24]	United States[25]

The chloroform constants according to various editions of the *United States Pharmacopoeia* are as follows:

Date.	Density at 15°.	Boiling point.
1851	1.49	142° F.
1869	1.490–1.494	140° F.
1873	1.480	142° F.
1882	1.485–1.490	60°–61° C.
1893	Not below 1.490	60°–61° C.

C. Regnauld[1] maintained that the specific gravity of chloroform is hardly a criterion of its purity, owing to conflicting results; but this statement was based upon the results of an examination of various samples of chloroform at a period prior to the adoption of improved methods of manufacture and purification, and before the formulation and recognition of more stringent pharmacopoeial standards. Specific gravity should not be regarded by any means as the *sole* criterion of purity; but the constant is indicative of the strength and, although to less degree, the purity of anaesthetic chloroform, and should always be determined.[2] For this purpose the pyknometer should be employed[3] and the determination should be made preferably at 15°. The Mohr-Westphal balance will serve to give a rapid approximate result, but should not be depended upon where any considerable degree of accuracy is desired. Chloroform is quite sensitive to temperature variations, but owing to the fact that it is considerably less volatile than ether, as well as comparatively non-hygroscopic, the determination of its density does not present such difficulties as are often encountered in the case of ether.

2. BOILING POINT.

A. The boiling point of chloroform was first deter-

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[1] The method of purification used was as follows: 500 cc. of chloroform containing 0.77 per cent. of absolute ethyl alcohol and 0.04 per cent. of water, but otherwise pure, were agitated with 1 liter of water repeatedly throughout one day; the water was then removed, and the treatment was repeated twice in the dark. The separated chloroform was then shaken with 500 cc. of water throughout one day, and finally with two successive portions of 250 cc. It was then dried over fused calcium chloride, and afterwards agitated with $^1/_5$th its volume of concentrated sulphuric acid, when to our surprise—for the chloroform had originally afforded no coloration with sulphuric acid, and the process of purification had so far been conducted in the dark—the acid assumed a yellow color. It was therefore found necessary to continue the treatment with sulphuric acid, until the chloroform failed to color it, to accomplish which three successive treatments were necessary. The chloroform was then tested for the presence of alcohol by the chromic acid, iodine, iodoform, and fuchsine tests (see *Alcohol*), and was found to be alcohol-free. It was accordingly agitated with 75 g. of anhydrous sodium carbonate during three days, separated by filtration, and 400 cc. were fractionated. The chloroform almost completely distilled over between 61.2° and 61.8°, and all above 62° (about 5 cc.) was eliminated. After refractionation, the chloroform was carefully examined and was found to be free from alcohol, water, acetaldehyde, and decomposition products: it gave no coloration with formalin-sulphuric acid.

[2] See *Alcohol.*

[3] No reference is made in the table to chloroform intended for industrial purposes.

[4] *Farmacopea Oficial Espanola*, **1905**, p. 198.

[5] Hirsch's "Universal-Pharmakopöe," **1**, 162 (1902).

[6] At 18°. *Nueva Farmacopea Mexicana*, **1904**, p. 477.

[7] *Pharmacopoea Helvetica*, **1907**, p. 101. Formerly 1.485–1.490.

[8] Hirsch, *Loc. cit.*

[9] *Farmacopea Chilena*, **1886**, p. 147.

[10] *Codex Medicamentarius Gallicus*, **1908**, p. 148. The specific gravity given is that specified for "Chloroforme Officinal;" it is stated that "Chloroformium Depuratum" possesses a density of 1.495–1.500, depending on its purity.

[11] Hirsch, *Loc. cit.*

[12] *Pharmacopoea Germanica*, **1900**, p. 86; *Deutsches Arzneibuch*, **1910**, p. 118. It is of interest to note here that in 1865 the *Ph. Hessen* specified chloroform of the density 1.515 at 17.5°, and that the *Ph. Hannover* stated the density 1.48.

[13] *Pharmacopoea Danica*, **1907**, p. 94.

[14] *Pharmacopoea Hungarica*, **1909**, p. 73.

[15] Hirsch, *Loc. cit.* The *Pharmacopoea Norvegica*, **1879**, p. 61, specifies 1.485–1.493.

[16] *Pharmacopoea Svecica*, **1908**, p. 76.

[17] *Pharmacopoea Fennica*, **1885**, p. 48.

[18] *Pharmacopoea Belgica*, **1906**, p. 65. Formerly 1.491 at 17°.

[19] *Pharmacopoeia of Japan*, third edition, **1907**, p. 84.

[20] *Pharmacopoea Austriaca*, **1889**, p. 61. Squire gives 1.485–1.490.

[21] Squire's *Companion to the British Pharmacopoeia*, **1908**, p. 373. The *Farmacopea Italiana*, fourth edition, p. 1357, gives 1.49.

[22] *British Pharmacopoeia*, **1908**, p. 75. In 1868 a *Pharmacopoeia of India* was issued; in this work the density 1.49 was specified (p. 266).

[23] *Pharmacopoea Nederlandica*, **1905**, p. 90. The density given is that of the "Chloroformum ad narcosin" (chloral chloroform); "Chloroformum" (0.6–1.0 per cent. alcohol) is stated to possess a specific gravity of 1.485–1.489.

[24] Squire, *Loc. cit.* The *Pharmacopoea Russica*, **1880**, p. 110, gave 1.485–1.490. Hirsch (*Loc. cit.*) gives 1.485–1.489.

[25] *Pharmacopoeia of the United States of America*, 8th revision, p. 99.

[1] *J. pharm. chim.*, [4] **29**, 402.

[2] As a rule, the specific-gravity determination is indicative of the amount of alcohol in chloroform, although such chloroform must, of course, always be examined for the presence of impurities and decomposition products. These points will be discussed in the course of the paper, under the various probable impurities. On the effect of alcohol on the density of chloroform, see *Alcohol.*

[3] The form of pyknometer designed by Perkin (*J. prakt. Chem., N. F.*, **31**, 486) is very suitable, although we have found the Sprengel pyknometer satisfactory.

mined by Liebig[1] who found the constant 60.8° C., and by Guthrie,[2] who, although he obtained a purified product of practically the same density as that of Liebig, stated that "absolutely pure chloric ether" boils at 74.4° C., a result doubtless attributable to the method of determination employed. Pierre,[3] in 1851, also obtained a high result—63.5° at 772.52 mm.—due, for the most part, to the impure chloroform employed in the determinations he conducted. In 1854, the boiling point of chloroform was given as 62°,[4] the same constant being given in 1861;[5] and although the determination of Regnault,[6] namely, 60.16° at 760 mm., had received recognition three years previously, we find it stated in 1866 that the boiling point of chloroform is 63°.[7] The constant found by Regnault appears to have been widely accepted as late as 1880; but the mean determination of Thorpe,[8] 61.2°, later supplanted it and is now given by various authorities.[9] The mean of the maximum (61.21°) and minimum (61.19°) of the recent accurate determinations of Timmermans[10] is 61.20°, the correct boiling point of pure chloroform.[11]

Other determinations of the boiling point of chloroform are as follows:

Year.	Observer.	Temperature.
1883.........	Schiff[12]	60.9° at 754.3 mm.
1884.........	Perkin[13]	62.0° at 760 mm.
1885.........	Bauer[14]	61.0° at 760 mm.
1899.........	Thayer[15]	61.6° at 760 mm. 61.64° at 760 mm.
1899.........	Petit[16]	61.97° at 760 mm.
1904.........	Wade and Finnemore[17]	61.15° at 760 mm.

B. The boiling points of the chloroforms recognized as official by the various pharmacopoeias are given in Table III. In general, it may be said that no specific directions are given for the determinations of the constant,[18] and that the influence of the variables (alcohol and water, in particular) on the boiling point has received very little attention.

C. Opinions are divided as to the value of the boiling-point determination as a criterion of the purity of anaesthetic chloroform. It has been stated that it is a valuable indication of the purity, since the presence of 0.5 per cent. of alcohol reduces the boiling point to "59.8° or 60°" and owing to the fact that a boiling point higher than "61°" indicates the presence of amyl or butyl compounds,[1] while Arzberger[2] has pointed out that in the determination of the boiling point of chloroform it is important that the distillation be continued until the last drops have been vaporized and that a perceptible rise of temperature at this point indicates the presence of water. Brown, however, expressed the opinion that the determination of the boiling point has little value so far as estimating the impurities of commercial chloroform is concerned.[3] Others have obtained anomalous results in attempting to determine the constant.[4]

TABLE III.—BOILING POINTS ACCORDING TO THE VARIOUS PHARMACOPOEIAS.

59.5– 61.5°.	60°.	60.8°.	61°.
Sweden[5]	Italy[6]	Spain[7] France[8] Chili[9] Roumania[10]	Mexico[11] Greece[12]
60–61°.	60–62°.	61.3°.	61–62°.
United States[13] Russia[14]	Great Britain[15] Germany[16] Austria[17] Switzerland[18] Belgium[19] Denmark[20] Norway[21] Japan[22] Finland[23]	Holland[24]	Hungary[25]

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[1] *Loc. cit.* The same value was later reported by Regnault (*J. pharm. chim.*, [4] **29**, 402.)

[2] *Loc. cit.*

[3] *Ann. chim. phys.*, [3] **33**, 199.

[4] Limprecht, "Lehrbuch der Organischen Chemie," p. 161.

[5] Kolbe, "Ausfuhrliches Lehrbuch der Organischen Chemie," Vol. I, p. 589.

[6] *Compt. rend.*, **39**, 301, 345, 397; see particularly, *Jahresber.*, **1863**, 70.

[7] Sharples, "Chemical Tables," p. 69.

[8] *Trans. Chem. Soc.*, **37**, 196.

[9] *E. g.*, Beilstein; Landolt-Börnstein.

[10] *Bull. soc. belg. chim.*, **24**, 244. Timmermans found that the variation *dt/dp* of the b. p. for 10 mm. pressure is 0.36°.

[11] The absolutely pure chloroform prepared by the authors possessed this boiling point, as determined by the arrangement of Berthelot and corrected to normal.

[12] *Ann.*, **220**, 95.

[13] *Trans. Chem. Soc.*, **45**, 530.

[14] *Ann.*, **229**, 163.

[15] *J. Phys. Chem.*, **3**, 37.

[16] *Ibid.*, **3**, 351. Petit purified the chloroform used by washing it twelve times with water, then shaking it with a concentrated solution of calcium chloride. The chloroform was then fractioned through a Hempel column, and the part kept was that distilling over between 60° and 60.3° at 741 mm. The corrected boiling point of this fraction was found to be 61.97°, much higher than recently reported. The impurity causing this high boiling point was not discovered by Petit.

[17] *Trans. Chem. Soc.*, **85**, 946.

[18] Exceptions are the *Pharmacopea Nederlandica*, 1905 [*J. pharm. chim.*, **23**, 479 (1906); *Chem. and Drug.*, **69**, 828] and the *Pharmacopea Austriaca*, 8th revision, p. 25.

[1] Allen, "Commercial Organic Analysis," Vol. I, 236. Cf. Hager, *Pharm. Z. Russland*, September, **1869.**

[2] *Pharm. Ztg.*, **51**, 321.

[3] *Pharm. J.*, March 19, 1892.

[4] For example, Werner (*Archiv. Pharm.*, [iii] **12**, 481) stated that chloroform boils over a naked flame at 62–63°, but that it does not boil below 64° on a water bath and often not until a temperature of 66° has been reached. In the latter case, Werner found that it was difficult to determine whether the liquid was boiling, as the surface showed no signs of ebullition. By immersing a piece of string in the chloroform to be distilled Werner found the difficulty was removed(!).

[5] *Pharmacopoea Svecica*, **1908**, p. 76

[6] *Farmacopea Italiana*, fourth edition, p. 1357. Hirsch gives 61–62°.

[7] *Farmacopoea Oficial Espanola*, **1905**, p. 198.

[8] *Codex Medicamentarius Gallicus*, **1908**, p. 148. The boiling point given is that specified for "Chloroforme Officinal," or "Chloroformum pronarcosi;" the boiling point of "Chloroformium depuratum" is stated to be 61°.

[9] *Farmacopoea Chilena*, **1886**, p. 147.

[10] Hirsch's *Universal-Pharmakopöe*, **1**, 162 (1902).

[11] *Nueva Farmacopea Mexicana*, **1904**, p. 477. At 76 cm. pressure.

[12] Hirsch, *Loc. cit.*

[13] *Pharmacopoeia of the United States of America*, 8th revision, p. 99.

[14] *Pharmacopoea Russica*, **1880**, p. 110. This is the latest edition of the work we have seen, but Hirsch (*Loc. cit.*) gives 60–62°.

[15] *British Pharmacopoeia*, **1908**, p. 75.

[16] *Pharmacopoea Germanica*, **1900**, p. 86; *Deutsches Arzneibuch*, **1910**, p. 118.

[17] *Pharmacopoea Austriaca*, **1889**, p. 61.

[18] *Pharmacopoea Helvetica*, **1907**, p. 101.

[19] *Pharmacopoea Belgica*, **1906**, p. 65.

[20] *Pharmacopoea Danica*, **1907**, p. 94.

[21] Hirsch (*Loc. cit.*). The *Pharmacopoea Norvegica*, **1879**, p. 61, gives 60–63°.

[22] *Pharmacopoeia of Japan*, third edition, **1907**, p. 84.

[23] *Pharmacopoea Fennica*, **1885**, p. 48.

[24] *Pharmacopoea Nederlandica*, **1905**, p. 90. The value given is that specified for "Chloroformum ad narcosin" (chloral chloroform); "Chloroformum" containing 0.6–1.0 per cent. of alcohol is stated to boil at 60° (62 cm.).

[25] *Pharmacopoea Hungarica*, **1909**, p. 73. In this place it may be noted that the *Pharmacopoea Croatico-Slavonica*, **1888**, p. 163, specifies "Chloroformium e chloralo," boiling point 60–61°.

While it is true that in the ordinary method of fractionation, any impurities decomposable by sulphuric acid and chlorinated decomposition products are concentrated in the residue and may then be recognized,[1] in the opinion of the authors the boiling-point determination is not a criterion of the purity of anaesthetic chloroform, unless either (*a*) pure chloroform—that is, absolute chloroform—is specified, or (*b*) the amount of alcohol (and water) added is definitely fixed and no range of addition, such as 0.4–1.0 per cent., is permitted. In any case, definite directions should be given in order that a standard method of determination would be employed.

When anaesthetic chloroform is distilled, the temperature rises immediately to about 55.5°, at which temperature water passed over with part of the alcohol present and some chloroform; the remainder of the alcohol distils over with part of the chloroform between 59.4° and 61°.[2] For example, the careful fractionation of 500 grams of anaesthetic chloroform made from acetone, containing 0.5 per cent. of alcohol and 0.026 per cent. of water, but otherwise pure, gave the following results:

Temperatures.	Weight of fraction. Grams.
55.5–59.4°	10
59.4–61.0°	177
61.0–61.2°	300
Above 61.2°	13

According to Wade and Finnemore,[3] the possible components of constant boiling point which may be isolated from a mixture of chloroform, alcohol and water are as follows:

Constituent.	Boiling point.	Per cent. chloroform.
Chloroform-alcohol-water	55.5°	92.5
Chloroform-water	56.1°	97.5
Chloroform-alcohol	59.4°	93.0
Chloroform	61.2°	100.0
Alcohol-water (95.5 per cent. alcohol)	78.15°	...
Alcohol	78.3°	...
Water	100.0°	...

Of these seven constituents, the first five may be separated from anaesthetic chloroform containing 0.5 per cent. of alcohol and 0.026 per cent. of water, and the authors have identified the first and third in samples of anaesthetic chloroform containing alcohol varying from 0.5–1.0 per cent.[4] In some cases, it was observed that the first constituent becomes turbid.[5]

It is therefore apparent that the variables of anaesthetic chloroform render the determination of its boiling point of no value as a criterion of purity, since we have here a mixture and no definite compound.

VI. The Decomposition of Chloroform.

1. THE CHANGES WHICH CHLOROFORM UNDERGOES UPON EXPOSURE TO AIR.

There has been considerable diversity of opinion among chemists as to the nature and products of the decomposition of chloroform; in fact, this discordance dates from the introduction of chloroform as an anaesthetic and prevails to-day. This condition is ascribable to the many influencing factors occasioned by the degree of purity of the chloroform under examination, the extent and nature of the exposure; but is principally due to the failure to consider, and therefrom to correctly interpret, the role of the general variable, alcohol, and with it the accompanying moisture.

In 1848, Morson[1] found that "pure" chloroform underwent decomposition in the presence of light and air, chlorine, hydrochloric acid, and probably other "chlorine compounds" being formed;[2] later he observed that the decomposition was variable in extent and rapidity, and that chloroform, when kept under water, did not decompose.[3] Maisch,[4] however, stated that chloroform containing moisture always showed the presence of "free chlorine" much sooner than dry samples.

Hager,[5] investigating the question more extensively, concluded that "pure" chloroform was not decomposed by the action of light alone; but that when chloroform is exposed to the action of the sun's rays, it decomposed, exhibited an acid reaction to test paper, and there were found, among its products of decomposition, hydrochloric acid, "chloroxycarbonic acid,"[6] formic acid,[7] and free chlorine. Hager first pointed out that chloroform was decomposed when air had access to it, even in the dark, although then very slowly.[8] Rump[9] made similar observations, having learned that protection from light does not prevent the decomposition of chloroform; he concluded that the smallest quantity of moisture and air would, in time, induce decomposition, and that this, once started, proceeded with increased rapidity. Under these conditions, by excluding the light, Rump found that carbonyl chloride would result.

In 1882, Regnault[10] pointed out that carbonyl chloride was the most dangerous impurity found in

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[1] Based on these observations, the authors have devised an extremely sensitive test for the detection of such impurities. This will be given when the tests for impurities are discussed.

[2] Cf. Wade and Finnemore, *Loc. cit.*

[3] *Loc. cit.*

[4] The alcohol was determined by the method of Nicloux (see *Alcohol*).

[5] The presence of water was established by means of calcium carbide (see *Water*).

[1] *Pharm. J.*, **8**, 69.

[2] Therefore, Morson suggested the test with litmus paper and purification by repeated agitation with distilled water.

[3] *Ibid.*, 279. In 1850 (see *Trans. N. Y. Acad. Med.*, **1**, 146), it had been observed in this country that chloroform becomes acid and contains "chlorinated oils" through decomposition.

[4] *Proc. Am. Pharm. Assn.*, **1866**, 264. Chloroform of the density 1.492, dried by means of calcium chloride, was kept in absolutely dry bottles and in bottles slightly moist, then both kinds were exposed to diffused daylight and to direct sunlight. Maisch concluded that the entire absence of water would not be sufficient to preserve the chloroform unaltered.

[5] *Pharm. Z. Russland*, September, 1869.

[6] Personne found that samples of chloroform liable to decomposition always contains "chlorocarbonic ether." It has also been maintained that the change is attributable to the presence of allylene dichloride.

[7] Kappeler (*Anaesthetica*, p. 173) stated that formic acid and aldehyde are products of the decomposition of chloroform.

[8] Hager found that chloroform, even if it does not exhibit an acid reaction, may be in a state of decomposition, and that this condition may be detected by the reaction such chloroform exhibits with ammonia, which then yields with it vapors of ammonium chloride.

The results of Hager's investigation gave rise to the statement which has persisted in the literature till to-day, namely, that specimens of chloroform, originally of good quality on keeping become impregnated with hydrochloric, hypochlorous, and formic acids.

[9] *Archiv. Pharm.*, October, 1874.

[10] *J. pharm. chim.*, [5] **5**, 504.

chloroform, and stated that it was produced in the presence of light by the action of air on chloroform.[1] In collaboration with Roux, Regnault demonstrated the formation of carbonyl chloride from chloroform in several different ways: By the action of the spark from an induction coil on a mixture of chloroform vapor and air; by allowing air saturated with the vapor of chloroform to circulate in an effluve apparatus;[2] and by the action of ozonized air. The last experiment showed that the production of carbonyl chloride was independent of the thermal and electric phenomena of the other two, and, along with the work of Rump, established the formation of carbonyl chloride during the oxidation of chloroform. Confirmation of this was later had from the investigations of Marty[3] and Stark.[4]

As to just what are the other products of the decomposition of chloroform, is a question which has received considerable, although not very discriminating, attention. Brown[5] found that while chloroform was not decomposed by the action of sunlight in the absence of oxygen, it was so decomposed when oxygen was present, yielding as products *chlorine*, carbonyl chloride, and water:

$$4CHCl_3 + 3O_2 = 4COCl_2 + 2H_2O + 2Cl_2;$$
$$2COCl_2 + 2H_2O = 2CO_2 + 4HCl.$$

These equations have been recognized as correct by Schacht and Biltz,[6] and by Adrian;[7] but Schacht and Biltz considered it necessary to add that they applied exclusively to the decomposition of chloroform which was perfectly free from alcohol. That the decomposition of chloroform is accelerated in an atmosphere of pure oxygen, is a fact which Schacht and Biltz were disposed to ascribe to the absence of nitrogen. At one time they appear to have entertained the idea that ozonization of the oxygen in contact with chloroform and under the influence of sunlight might cause decomposition, but experiments made in reference to this point in 1868, wherein it was shown that no ozonization occurred under such conditions, seem to have induced a contrary view.

In regard to the ultimately recognizable results of the oxidation of chloroform in particular instances—for example, in the case of anaesthetic chloroform—there is one circumstance which exercises a decided determining influence; but, as indicated by Schacht and Biltz,[1] it is not always sufficiently considered, and this fact has given rise to differences of opinion as to the nature of this decomposition and of its products. For instance, Ramsay[2] advanced the opinion that the only products of the decomposition of chloroform are carbonyl chloride and hydrochloric acid, while Brown, Schacht and Biltz, and Adrian maintain that in addition to the formation of those products there is also an elimination of chlorine in the free state. Schacht and Biltz considered that this difference of opinion was doubtless to be ascribed to want of attention to the presence of alcohol in the chloroform experimented with,[3] and to the resulting misinterpretation of the chemical changes which occur. They stated that they had succeeded in proving that the well-known influence of alcohol in preserving chloroform from decomposition[4] was due to the alcohol taking up and chemically combining with the deleterious products resulting from the decomposition, so as to render them innocuous. Later,[5] they concluded that, though the direct products of the decomposition of "pure" chloroform were only chlorine[6] and carbonyl chloride, in the case of chloroform containing alcohol the chlorine thus eliminated acted on the alcohol present, and so gave rise to the production of hydrochloric acid. In this way they accounted for the presence of hydrochloric acid in the first stage of the decomposition of anaesthetic chloroform,[7] and considered that they had explained the point which had given rise to dispute, namely, that the elimination of free chlorine is a primary feature of the alteration. These views led to a controversy with the Browns,[8] and the formation and presence of

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[1] Regnault considered the accidental presence of carbonyl chloride common at that time.

[2] Regnault and Roux found that nitrogen charged with the vapor of chloroform also decomposed the chloroform in an effluve apparatus, the products being hydrochloric acid and a mixture of C_3Cl_8 and C_4Cl_6. Cf. the results of Besson and Fournier (*Compt. rend.*, **150**, 1118) on the action of the silent discharge on chloroform in the presence of hydrogen; among the chlorinated derivatives separated were CCl_4, C_2Cl_4, C_2HCl_5, C_2Cl_6, C_3Cl_6, C_3HCl_7, and C_4Cl_8. Cf. Regnault, *Ann.*, **33**, 310; *Ann. chim. phys.*, [2] **71**, 353.

[3] *L'Union Pharm.*, November, 1888. Marty found that "pure" chloroform did not remain unaffected more than two days in summer or 5 days in winter, when freely exposed to air. The same chloroform remained unaltered for 15 months in the dark, although in contact with air. With chloroform containing 0.1 per cent. of absolute alcohol, no decomposition resulted even after an exposure of 15 months to continuous sunlight.

[4] *Pharm. J.*, [3] **20**, 407. Chloroform exposed to diffused sunlight for 5 months contained hydrochloric acid, carbonyl chloride, and an "oily hydrocarbon." According to Stark, the alarming dyspnoea produced by some samples of chloroform when inhaled is probably due to the presence of carbonyl chloride (see *Effects of Impurities*, Section VII, 2).

[5] *Pharm. Soc. Ednb.*, March, 1893.

[6] *Pharm. J.*, **1893**, 1005.

[7] *J. pharm. Chim.*, **18**, 5.

[1] *Loc. cit.*

[2] *J. Soc. Chem. Ind.*, **11**, 772. The same view was held by Breteau and Woog, *Compt. rend.*, **143**, 1193.

[3] See *Preservation.*

[4] The correctness of this view, which has been generally favored, will be fully considered under *Preservation.*

[5] *Pharm. J.*, [3] **22**, 1041.

[6] Popov (*J. Russ. Phys.-Chem. Soc.*, **7**, 1061) studied the influence of light on chloroform dissolved in linseed oil, finding that the iodine number of the oil was lowered, owing to the action of the halogen upon the unsaturated compounds of the oil. This work does not, however, prove that chlorine is a product of the photolytic decomposition of chloroform.

[7] Cf. Laurent (*Ann. chim. phys.*, **1837**, 318), who found that chlorine acts on chloroform in the sunlight forming hydrochloric acid and "C_2Cl_8." The opinions of Schacht and Biltz, variously expressed, seem to embody this general view: The gradual disappearance of free chlorine when chloroform is undergoing decomposition is an indication of its further action on the chloroform, producing hydrogen chloride and altering the relative proportions of carbonyl chloride and hydrogen chloride so as to increase the latter.

[8] Schacht and Biltz (*Pharm. J.*, [3] **23**, 1005) stated that "decomposition cannot be detected in alcohol-reduced chloroform until all the added alcohol has been consumed." Brown (*Ibid.*, **24**, 321) found that "pure" chloroform to which 0.077 per cent. of alcohol had been added, when exposed to direct sunlight in colorless glass, began to decompose in 14–19 days. He found that after decomposition had been recognized by zinc iodide and starch, as well as baryta water, reactions were obtained with 1:2000 potassium dichromate solution and the iodoform test, and these were ascribed to the presence of alcohol. Schacht (*Ber. pharm. Ges.*, October, 1894) defended his position, and stated that the reactions obtained were not produced by alcohol, but by "chloric ether" and "phosgene alcoholide." The Browns (*Pharm. J.*, [3] **25**, 836) maintained that Schacht had not proved that ethyl chloride and chloroformic ether were produced in the decomposition of "alcohol-reduced chloroform," and that they gave reactions similar to alcohol. On the other hand, they considered that they themselves had proved that at the time the decomposition

free chlorine as one of the decomposition products of chloroform containing alcohol were by no means definitely settled.

Schoorl and van den Berg[1] conducted quantitative experiments which seemed to indicate that when chloroform was decomposed by the action of light in the presence of an excess of oxygen, carbon dioxide, water, and chlorine were formed in accordance with the following equation:

$$2CHCl_3 + 5O \longrightarrow 2CO_2 + H_2O + 3Cl_2$$

According to the same chemists, when insufficient oxygen is present—a condition usually obtaining in practice—carbonyl chloride and hydrogen chloride are produced in molecular proportions:

$$CHCl_3 + O = HCl + COCl_2.$$

The equations given by Schoorl and Van den Berg were evidently intended to apply to the decomposition of pure chloroform, and the changes which occur in anaesthetic chloroform were apparently not considered. Schoorl and Van den Berg[2] confirmed the observation that in the absence of air or oxygen, chloroform is not affected by light exposure.

Finally, Dott[3] has suggested that the formation of carbonyl chloride in chloroform very probably occurs in accordance with the following equation:

$$CHCl_3 + H_2O_2 = COCl_2 + HCl + H_2O.^4$$

Summary of the Present Knowledge of the Decomposition of Chloroform.

From these investigations one may conclude that chloroform free from alcohol, when exposed to air and light, will begin to decompose in a short time; but that this is dependent upon the conditions of exposure—upon the amount of air present and upon the intensity of the light. Consequently the effects produced vary, and chloroform which in one experiment has been found to show decomposition within several hours may, at another time, require an exposure for a whole day, or longer, to full sunlight, before it shows the first indications of decomposition. The temperature prevailing during the period of exposure is also an important consideration. Then again, the nature of the container is of considerable effect in either inducing or retarding decomposition; for instance, in the case of glass, color and solubility should be carefully considered. Details as to these points are usually lacking.

The products of the decomposition of "pure" chloroform, according to various investigators, may be thus summarized:[1]

Chlorine, hydrogen chloride..........	Morson, Maisch, and Hager.
Carbonyl chloride....................	Rump, Regnault.
Carbonyl chloride, hydrogen chloride..	Stark, Ramsay, Schoorl and Van den Berg, and Dott.
Carbonyl chloride, chlorine...........	Brown, Schacht and Biltz, and Adrian.

The formation of carbonyl chloride is alone definitely agreed upon.

The decomposition of chloroform has been universally conceded to be an oxidation process. It is generally accepted that chloroform is unaffected by light alone, and that light, although it accelerates oxidation, is not a necessary factor in the process (Hager, Rump, Brown, Schoorl and Van den Berg); however, several investigators appear to have inclined to the view that light is essential, although in noncommittal language, merely stating that it favors decomposition (Regnault, Dott).

If we except the obvious action of water on carbonyl chloride, the influence of moisture on the process of oxidation is still unsettled. In most of the investigations which have been conducted, the presence of water has not been considered; but when taken into account, it has generally been thought to accelerate the decomposition (Maisch, Rump, Dott), although Morson took a contrary view. This consideration is of importance on account of the presence of water in anaesthetic chloroform and, although to much less degree, in the air, and in view of the hydrogen dioxide theory of Dott.

With regard to the changes which occur in anaesthetic chloroform during exposure to air and light, there exists a decided diversity of opinion, principally owing to the fact that no examinations were made during the course of the various investigations, so far as we are aware, for the presence of the oxidation products of alcohol in such chloroform, and the exact role of alcohol in preservation has been consequently misunderstood. Chemists who have studied this phase of the decomposition of chloroform (Schacht and Biltz) have considered that the decomposition is normal, except that hydrochloric acid is formed by the action of chlorine on the alcohol present.

It therefore seemed to the authors that the whole subject required investigation, and accordingly an experimental study of the decomposition of both pure and anaesthetic chloroform was carried out, with particular reference to the following phases of the problem:

1. What are the exact products of the oxidation of pure chloroform?
2. What are the nature and products of the oxidation of anaesthetic chloroform?
3. What part does water play in both cases?

It was thought that the solution of these questions would throw light on, if not fully explain, the role of alcohol and other substances in the so-called pre-

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was first recognized by means of zinc iodide and starch, chlorine had not been produced in sufficient quantity to combine with all of the added alcohol, and that ethyl chloride, chloroformic ether or carbonic ether did not give reactions which could be mistaken for those of alcohol.

[1] *Pharm. Weekblad*, **42**, 877. See also the recent experiments of Benrath (*Ann.*, **382**, 222), who found that under the influence of light, and in the presence of water and air, chloroform formed carbonyl chloride and hydrogen chloride.

[2] *Ibid.*, **43**, 8. On exposure to air, in the absence of light, chloroform gave no precipitate with silver nitrate even after four hours, whereas bromoform and iodoform after one hour gave distinct indications of decomposition.

[3] *J. Soc. Chem. Ind.*, **27**, 272.

[4] Support to this view is had from the fact that conditions which favor the formation of hydrogen dioxide—a degree of moisture and direct sunlight—are also those which favor the decomposition of chloroform.

[1] The reported occurrence of "chlorinated oils" (Gibbs; Stark) and of similar products of the decomposition of impure chloroform is not considered in this summary.

Sample.	No. 1 (Pure).	No. 2 (Pure).	No. 3 (Pure).	No. 4 (Pure).	No. 5 (Pure).	No. 6 (Pure).	No. 7 (Anaes.).	No. 8 (Anaes.).
Description.	35 g. pure chloroform in a 2-oz. bottle of anactinic glass. Exposed 18 days.	A colorless 50 cc. glass, half full of pure chloroform. Exposed, 18 days; pungent foreign odor.	10 cc. of pure chloroform in a colorless 100 cc. glass bottle. Exposed 22 days.	100 cc. pure chloroform in a colorless 250 cc. glass bottle. Exposed 22 days.	50 g. pure chloroform in a 5-oz. bottle of anactinic glass. Exposed 23 days.	20 g. pure chloroform and 5 g. water in a 50 cc. colorless bottle. Exposed 18 days.	100 cc. chloroform of density 1.49 over 25 cc. conc. H_2SO_4 for 38 days in a 1-lb. brown glass bottle.	A 100 gr. colorless glass bottle 1/2 full of chloroform containing 0.25% alcohol. Exposed 17 days.
$COCl_2$	Trace	Decided reaction	Decided reaction	Marked reaction; sample fumed in air	Faint reaction; slight odor	None	Very pronounced reaction; sample fumed in air	None
HCl	Evidently present	Present	....	Present	Present	Present in both water and chloroform	Present	None
Grams of acid, calculated as HCl, in 100 cc. of sample	0.00032	....	0.004	0.4417	0.0023	Chloroform: 0.0022	0.1440	....
Cl	None	Present	....	Present	See remarks	....	None	None
Aldehyde	None	None	....	None	....	....	....	None
Acetic acid	None	....	....	....	....	....	....	Present
Grams of acid, calculated as acetic, in 100 cc.	....	....	....	....	....	....	....	0.00045 gram increase
Sulphuric acid test	....	....	....	....	....	....	....	Negative
"Chlorinated decomposition compounds"	....	....	....	....	....	....	....	None
"Odorous decomposition products"	....	....	....	....	....	....	....	None
Hydrogen dioxide	None	None	....	None	....	Trace in water	None	None
Remarks	Products: Carbonyl chloride, and probably HCl. Cf. No. 2	Products: Carbonyl chloride, HCl and Cl. Cl discriminated from H_2O_2 by mercury and chromic acid test	....	Absence of H_2O_2 shown by vanadic acid test. Presence of Cl proved	Mercury test indicated Cl or H_2O_2; neither found by other tests. Reaction could be ascribed only to carbonyl chloride	....	Decomposition due to removal of alcohol present by sulphuric acid. Chloroform became turbid; this was dispelled by agitation with an equal volume of alcohol and acidity became 0.096 gram after 3 hours	Alcohol alone oxidized.

Sample.	No. 9 (Anaes.).	No. 10 (Anaes.).	No. 11 (Anaes.).	No 12 (Anaes.).	No. 13 (Anaes.).	No. 14 (Anaes.).	No. 15 (Anaes.).	No. 16 (Anaes.).
Description.	50 cc. of pure chloroform, containing 1% alcohol, exposed 31 days in a colorless bottle of 120 cc. capacity.	Two samples of chloroform containing 0.74% alcohol and 10% hydrochloric acid exposed for 34 days in colorless glass bottles (1/3 full).	Brown bottle half full of chloroform containing 0.74% alcohol and 0.118% water, exposed 35 days.	65 cc. of pure chloroform with 1.5% of alcohol and 10 cc. of 3.4% H_2O_2 exposed 40 days in a 200 cc. brown glass bottle.	50 g. of chloroform containing 0.25% alcohol and saturated with water, exposed for 50 days in a bottle totally filled.	50 g. of chloroform containing 0.25% alcohol under 10 cc. of water for 50 days in a 100 cc. colorless glass bottle.	Anactinic glass bottle full of pure chloroform containing 0.25% alcohol. Exposed 52 days.	A half-pound brown glass bottle of chloroform containing 0.97% alcohol, one-half filled. Examined after 177 and 222 days.
$COCl_2$	None	None in either sample	None	None	....	None in a free state	None	None in both cases
HCl	None	....	None	None	None	Present in water layer	None	None
Grams of acid, calculated as HCl, in 100 cc. of sample	....	....	....	....	....	....	....	....
Cl	None	None	None	....	....	None	None	None
Aldehyde	1: 3300	None	1 : 3200	1 : 1660	None	....	None	After 222 days, 1 : 3500
Acetic acid	Present	....	Present	Present	Present	....	Present	Present in both cases
Grams of acid, calculated as acetic, in 100 cc.	0.00022 gram formed during exposure	....	0.0002 gram formed during exposure	....	0.00015	0.00135 gram in chloroform layer	0.0006 gram	After 177 days, 0.0003; after 222 days, 0.00135
Sulphuric acid test	Very faint; intensified by formalin	....	Faint yellow color	Negative	....	Negative	....	....
"Chlorinated decomposition compounds"	None	....	None	None	....	....	....	....
"Odorous decomposition products"	....	....	None	None	....	....	....	....
Hydrogen dioxide	None	None	None	....	....	None	None	None
Remarks	Alcohol alone oxidized	Alcohol not consumed	Alcohol alone oxidized	Chloroform apparently not affected	Alcohol alone oxidized	Alcohol originally present consumed; therefore chloroform underwent decomposition. Alcohol added was insufficient under the conditions	Alcohol alone oxidized	Alcohol alone oxidized

Sample.	No. 17 (Anaes.).	No. 18 (Anaes.).	No. 19 (Anaes.).	No. 20 (Anaes.).	No. 21 (Anaes.).	No. 22 (Anaes.).	No. 23 (Anaes.).
Description.	A 2-oz. brown glass bottle 7/8 filled with chloroform containing 0.97% alcohol and saturated with water. 120 days.	A half-pound bottle (anactinic glass), 5/6 filled with chloroform containing 0.97% alcohol. Exposed 219 days.	A 2-oz. brown glass bottle 7/8 full of chloroform containing 0.97% alcohol. Exposed 220 days.	A 2-oz. brown glass bottle 3/4 full of chloroform containing 0.97% alcohol. Exposed 222 days.	A 2-oz. brown glass bottle 1/5 full of chloroform containing 0.97% alcohol. Exposed 222 days.	A 2-oz. anactinic glass bottle 4/5 full of chloroform containing 0.97% alcohol. Exposed 222 days.	An 8-oz. colorless glass bottle 1/4 full of chloroform containing 0.97% alcohol. Examined after 120 and 225 days.
$COCl_2$	None	None	None	None	None	None	None
HCl	None	None	None	None	None	None	None after 120 days; faint after 225 days
Grams of acid, calculated as HCl, in 100 cc. of sample	....	....	....	....	....	....	....
Cl	None	None. Negative result after 4 mos.	None	None	....	None	None
Aldehyde	....	1 : 4000	Trace	Trace	None	None	None detectable
Acetic acid	Present	Present	None	Present	Present	Not determined	Present in both cases
Grams of acid, calculated as acetic, in 100 cc.	0.00025	0.000675	....	0.00015	0.0009	....	....
Sulphuric acid test	.....	Decided reaction; intensified by formalin	....	Faint	....	Decided reaction	....
"Chlorinated decomposition compounds"	....	....	....	Faint	....	Faint reaction	....
"Odorous decomposition products"	....	....	....	None	....	None	....
Hydrogen dioxide	None	None	None	None	....	None	None
Remarks	Alcohol oxidized	Alcohol alone oxidized	Incipient oxidation of alcohol	Oxidation products of alcohol alone	Alcohol, but not chloroform, oxidized	Deportment with H_2SO_4 could be attributed only to oxidation products of alcohol	Alcohol completely oxidized

servation of chloroform, an exact explanation of which has been wanting.[1]

Experimental.—Various samples of both pure chloroform[2] and chloroform containing the usual pharmacopoeial amounts of alcohol and water, were exposed, in well-stoppered[3] containers of various sizes, and containing varying amounts of the samples, and of both colorless and anactinic glass, such as are customarily used in the trade, for different periods of time, but at room temperature (20° C.), from September to May, inside of a window having direct southern exposure. The conditions were extreme, but nevertheless were similar to those obtaining in many pharmacies and hospitals.

The anaesthetic chloroform used was examined prior to the experiments, and only such chloroform as was found to be free from all impurities was used. However, an amount of water equivalent, on the average, to 5.1 per cent. by volume of the alcohol was present.[4] Thus each sample was of pharmacopoeial grade.

The method of examination consisted in carefully applying, in duplicate whenever possible, the tests for the detection of the oxidation products of chloroform and alcohol. Whenever possible, the amount of these impurities was determined. The methods used will be detailed in the succeeding portions of this paper, as each impurity is considered.

The conditions and results of each experiment may be seen in the preceding table.

From these experimental results, as well as from others later to be detailed, the authors have arrived at the following conclusions:

1. The products of the oxidation of *pure* chloroform are carbonyl chloride and hydrochloric acid:

$$CHCl_3 + H_2O + O_2 = COCl_2 + HCl + H_2O_2;$$
$$CHCl_3 + H_2O_2 = COCl_2 + HCl + H_2O.$$

We are convinced that oxidation will not occur if water be excluded, and the absolute exclusion of moisture appears to be impossible. Hydrogen dioxide is formed, although we have been unable to detect it in chloroform undergoing oxidation and therefore conclude that its existence is ephemeral; and oxidation of the chloroform continues throughout the period of the exposure.[5]

The decomposition of pure chloroform is favored by a degree of moisture and is accelerated by light, as is shown by a comparison of the results obtained in the experiments wherein colorless glass was used with those in which anactinic glass containers were employed. Moreover, carbonyl chloride is formed with increased readiness in the presence of acids.[1]

The extent of the oxidation is dependent upon the nature of the container, the amount of air present, the purity of the sample, and the intensity of the light to which it is exposed. In light alone, when no air is present, no detectable decomposition occurs for ordinary periods of exposure; and in cases where there is air contact alone, and no exposure to light, the oxidation is slow.

Free chlorine can only result from the photochemical decomposition of carbonyl chloride:[2]

$$COCl_2 \longrightarrow CO + Cl_2.$$

It is likely that in the cases where "chlorine" was identified as an indication of incipient alteration of chloroform, hydrogen dioxide was the cause of the reactions observed. It will be observed that no chlorine was found by the authors when containers of anactinic glass were used.

This view of the oxidation of pure chloroform is supported in full by the conduct of such chloroform toward ozone[3] and certain oxidizing agents, as, for example, chromic acid,[4] in which case no free chlorine is formed, except possibly through a secondary reaction, and the products are water, carbonyl chloride, and chromyl chloride; and by the analogous case of the photochemical oxidation of iodoform,[5] the primary products of which are carbonyl iodide and hydriodic acid, free iodine resulting only from the decomposition of the carbonyl iodide and from the oxidation of the hydriodic acid. In the case of pure chloroform, the whole reaction is also the sum of a purely photochemical process, since, according to our experiences, free chlorine cannot result through the oxidation of chloroform itself, except from a secondary process, namely, from the decomposition of carbonyl chloride.

2. The products of the oxidation of anaesthetic chloroform are primarily the oxidation products of alcohol, and no decomposition of chloroform itself

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[1] See *Preservation*.

[2] This chloroform was prepared according to the method of the authors, already described, and we think that it was absolutely pure.

[3] No cork stoppers unprotected by metal caps were employed. In the experiments on pure chloroform, glass-stoppered bottles were solely used.

[4] The alcohol content of the anaesthetic chloroform used was determined quantitatively by the method of Nicloux (see *Alcohol*).

[5] On the formation of hydrogen dioxide when oxygen is enclosed over water and exposed to light, see Kharichkov, *J. Russ. Phys. Chem. Soc.*, **42**, 904; but see particularly Tian, *Compt. rend.*, **152**, 1072, and Chlopin, *J. Russ. Phys. Chem. Soc.*, **43**, 554.

[1] Cf. Lowry and Magson, *Trans. Chem. Soc.*, **93**, 121, who observed that the formation of carbonyl chloride is evidently accelerated by the presence of acids.

[2] In this connection, see Coehn and Decker, *Ber.*, **43**, 130; and Weigert, *Ann. Physik.*, [4] **24**, 55 (1907). The influence of light on the reversible reaction, $CO + Cl_2 \rightleftarrows COCl_2$, is purely catalytic.

[3] Erdmann (*Ann.*, **362**, 133) has demonstrated that ozone acts on chloroform as follows: $CHCl_3 + O_3 = COCl_2 + HCl + O_2$.

[4] In 1869, Emmerling and Lengyel (*Ber.*, **2**, 546) studied the oxidation of chloroform with sulphuric acid and potassium dichromate. They found but a small amount of carbonyl chloride among the products of oxidation, and incorrectly interpreted the results they obtained, inasmuch as they believed chlorine is formed: $2CHCl_3 = 2COCl_2 + H_2O + Cl_2$. Erdmann (*Ber.*, **26**, 1990) showed that the reaction which occurs is as follows:

$$2CHCl_3 + CrO_3 + O_2 = 2COCl_2 + CrO_2Cl_2 + H_2O.$$

In 1869, Schützenberger showed that carbonyl chloride is obtained in good yield by the action of sulphur trioxide on carbon tetrachloride. On the oxidation of chloroform with chromic acid, see also Cotton, *Bull. soc. chim.*, [2] **43**, 420. On the oxidation of carbon tetrachloride, see Schmidt's "Pharmaceutische Chemie," **2**, 148; and *Ber.*, **14**, 927.

[5] See Plotnikow, *Z. physik. Chem.*, **75**, 337, 385. According to this investigator, the whole reaction is as follows:

$$CHI_3 + O = COI_2 + HI; COI_2 = CO + I_2; 2HI + O = H_2O + I_2.$$

In the light, under constant conditions, the iodine separated is proportional to the time, and if the illumination is removed the reaction still proceeds, but with reduced velocity. There is no separation of iodine in the absence of oxygen, and none in a benzene solution which has not been exposed to light.

occurs while the oxidation of alcohol proceeds.[1] When the oxidation of alcohol reaches a maximum, decomposition of the chloroform goes on as in the case of pure chloroform, with the exception that chlorinated derivatives of the oxidation products of alcohol may result.

The retardation is dependent upon the amount of alcohol present—that is, the alcohol acts as a shunt through its capacity for oxidation.[2] The extent of the oxidation is, of course, subject to the conditions referred to under 1. It is important to note, however, that anaesthetic chloroform always contains water, the usual amount being about 0.05 per cent. by volume, according to our experiences.

3. At the inception of this investigation, it was considered possible that the instability of chloroform of all grades might be due to the presence of some catalytic agent, the removal of which would lead to beneficial results, as has been found in the case of sodium hypochlorite,[1] for example. Therefore, this possibility was carefully considered, even though the evidence to the contrary seemed to be of a convincing nature. It was ascertained that the oxidation of alcohol is accelerated by the presence of oxidizable bodies in solution and that foreign organic substances have a detrimental influence upon chloroform—which shows the necessity of having anaesthetic chloroform of a high degree of purity; but we have arrived at the conclusion that, given proper purification, the chloroform prepared from chloral hydrate, alcohol, acetone, or carbon tetrachloride is in all cases identical.[2] In the experiments just cited, only pure chloroform and anaesthetic chloroform were used.

(*To be continued in the May No.*).

LABORATORY AND PLANT

THE ADAPTION OF THE CENTRIFUGAL PUMP TO CHEMICAL PROBLEMS.[3]

By F. G. Wheeler.

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It has always seemed to me that the machine which is most used in chemical engineering is the one for moving liquids from one place to another, either from one tank to another or to circulate it through various devices for purposes best known to the user. It makes no difference whether the engineer wants to raise water from a mine or to discharge a sludge to a stream, the pump in some form is the most useful agent which can be applied. In all problems of this kind, that kind of a pump which has no valves and which depends alone upon centrifugal force to impart energy to the liquid has appealed to me as the best device which can be selected. As manufactured during the last few years, it moves the liquid with less loss of energy than any other device, stands more abuse and can be operated with cheaper labor than any other machine for this purpose. In the handling of water in quantities above 100 gallons per minute, it is replacing all kinds of steam pumps, except perhaps very large fly wheel engines. It can be used to pump solutions whether they are acid or alkaline, clear or muddy, viscous or mobile. In the use of the centrifugal pump for this chemical service, however, we must have a machine adapted for the heaviest kind of work. It must be built for severe duty from the day it is put into commission to the day it is thrown on the scrap heap.

In selecting a pump for service of this kind, we must consider first whether it will meet the conditions as well as any other device which we could use. I have found that in quantities above 100 gallons per minute the centrifugal will handle any liquid which will flow, or can be made to flow readily. The second point to be considered is first cost. In many instances the first cost of a machine will determine whether it can be applied. Because the centrifugal pump appeared simple, many manufacturers tried to meet all conditions with it, using the cheapest kind of a machine to compete with the steam pump, but it has been shown that it is as expensive to instal a good centrifugal pump at the present time as it is to instal a steam pump, but the former is thoroughly well built and a machine which can compete on the basis of efficiency.

Historically, the pump has been known since the eighteenth century, but the first designs were more like fans than pumps, and were both crude and inefficient. Up to the time when the water turbine was developed the laws which govern the working of a centrifugal pump were but meagrely known, and we have many pumps in operation to-day which were designed before the turbine was developed. When the laws which govern the operation of the reaction turbine were studied, it was learned that the centrifugal pump was in a general way a turbine run backward, and from this were designed various makes of

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[1] See *Preservation*.

[2] Additional support to this view is had from the action of pure oxygen on anaesthetic chloroform (q. v.) and supplementary evidence is given under *Preservation*.

[3] Read at the meeting of the American Institute of Chemical Engineers, Washington, December, 1911.

[1] The decomposition of commercial hypochlorite of soda is very largely due to the presence of small quantities of iron as ferrate in the liquor (Muspratt and Smith, *J. Soc. Chem. Ind.*, **1898**, 1096; **1899**, 210).

[2] Trillat (*Nouveaux Remedes*, **1904**, No. 13, 289; *Bull. gen. de Therap.*, **1904**, 46) arrived at a similar conclusion. He undertook to ascertain how chloroform prepared from chloral hydrate compared in point of purity with chloroform prepared from alcohol or acetone, and came to the conclusion that these kinds of chloroform are, after careful purification and rectification, absolutely equivalent. Trillat pointed out that foreign organic substances have an injurious influence upon chloroform, just as do water and air, and he ascribed the change to catalysis. The formation of carbonyl chloride, for instance, he found could be caused by mere contact with the human skin, and this suggested the possibility that it may arise from contact with the mucous membranes This is, however, still an open question, and is hardly supported by the work of Burkhardt (*Munch. med. Wochenschr.*, **1909**, 1678). Such decomposition refers, of course, only to pure chloroform or to such anaesthetic chloroform as contains only a mere trace of alcohol.

We have shown here the necessity of having chloroform of sufficient purity. The care required for its maintenance in an unaltered state will be discussed under *Storage*.

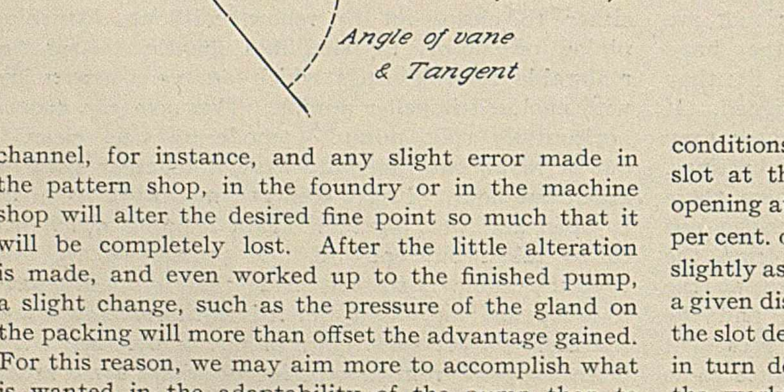
centrifugal pumps which operated much better than the old type. There were many difficulties still to be overcome, and it has been but a few years that we have had a really efficient, commercial machine, which competes with other devices because of real merit.

We are all familiar with the cheap centrifugal pump used by contractors and many factories at the present time. I have seen them used in excavations, quarries, paper mills and many other places. They have a two-piece shell, overhung from the support at one side. They are split vertically, and have a single suction on the side opposite from the support. An open fan-like impeller does the work, and enters the casing from the side of the support through a gland which acts like a bearing. It is claimed that this overhung casing has the advantage that the discharge can be turned in any direction. We shall all have to admit that it does have this advantage, which is really that of saving one ell. Its disadvantages are many. There is one modification of this which has a solid scroll and two side pieces, but the principle is the same. The single inlet causes an axial thrust toward the suction, and the first alteration in design was to make the machine with a double suction. This made the casing still further from the support, and to overcome the long overhang, another gland was placed on the outer end of the shaft. This I presume was to be used as a bearing to help support the shaft, but in pumps I have examined, the gland only wore out the outer end of the shaft, either from the vibration of the casing or the strain of the impeller. This overhung casing in some sand pumps was changed to one having a central support. This was considered severe service and it was thought the better method because it decreased the gland wear and helped keep the shaft in alignment. This central support has been almost universally adopted at the present time, but for many years the manufacturers retained the overhung casing as being of advantage in changing the direction of the discharge, and a much cheaper construction. There are still some of these casings used, even with more modern pumps. One maker used the suction pipes to support the casing, but I have seen only those of this one manufacturer supported in this way. All the pumps so far described, are inefficient, inaccessible and crude, because they have a minimum of machine work to make them fit; they are rough castings, thin, and poorly designed. If used for anything but the handling of water they quickly give out, requiring repairs or new castings. The wear on the shaft in the glands, where these were used as a bearing, caused the builders to put in outboard bearings, supported directly from the concrete foundation. Many, however, even at the present time, use the glands as bearings, and the shafts are lubricated in these glands with grease or oil. The next improvement of any importance came about when the laws were studied more closely: the open fan-like impeller was shrouded and finally supplanted by what is known as the enclosed or shrouded impeller. There were many modifications made by different manufacturers, such as the single suction, the double suction, and the double-single suction where the dividing vane came to the periphery. All worked upon the same principle: what entered at the hub must be discharged at the rim. This put more energy into the water, and not so much into friction. Between the sides of the impeller and the wall of the casing, the water revolves only half as fast as it does with the open impeller, because with the open impeller the clearance between the vanes and the sides must be a minimum, and the water must brush the sides as fast as the impeller revolves, where the closed impeller has greater clearance and the speed of the water divides itself between the revolving disc and the sides. This increases the efficiency, and also decreases the wear on the casing. It makes an efficient machine which can be built more easily than an efficient open impeller pump because the clearance need be at only one location. In an efficient open impeller pump, the casing and the sides of the vanes must be accurately machined to fit. With all of the open impeller pumps I have examined, however, the casing and the vanes were only as smooth as the castings fresh from the mold, and no attempt had been made to make the clearance particularly small. I have seen a clearance of over 1/4 inch, and the pump had an efficiency of 20 per cent. I have seen a six-inch pump in a paper mill, lifting about 1000 gallons per minute to a height of about 30 feet (which is about $7^1/_2$ horsepower) being driven by an 8-inch double-ply belt, which was so severely treated that the complaint concerning the pump was that they didn't seem to be able to keep belts on it. The speed of the belt was about 3000 feet per minute, and it should have been able to do 30 horsepower work easily. The only way in which a centrifugal pump with an open impeller can be made to work satisfactorily is to put on a large motor or engine.

The next improvement of noteworthy importance was the splitting of the shell horizontally. Many manufacturers at the present time do not do this, but it lends an advantageous accessibility to the pump. With the shell split in this manner the entire inside of the pump can be opened in a few minutes either to clean out or renew, without disturbing piping or motor. It simplifies greatly the use of renewable running rings which are very convenient with enclosed impeller pumps. Two men can open a horizontally split pump of moderate size, clean it out or renew the rings and have it together again in about one hour. I have seen two men work six hours to open and put together again a pump which has to be taken out endwise. Of course, we are told that the pump is so well made that it doesn't have to be opened very often, but it is not foreseen whether the user will get some chip, or nut or bolt in it; this often happens from new piping or where some repair is being made to an intake. Several of the manufacturers who once made the solid shell pump, are changing to the horizontally split.

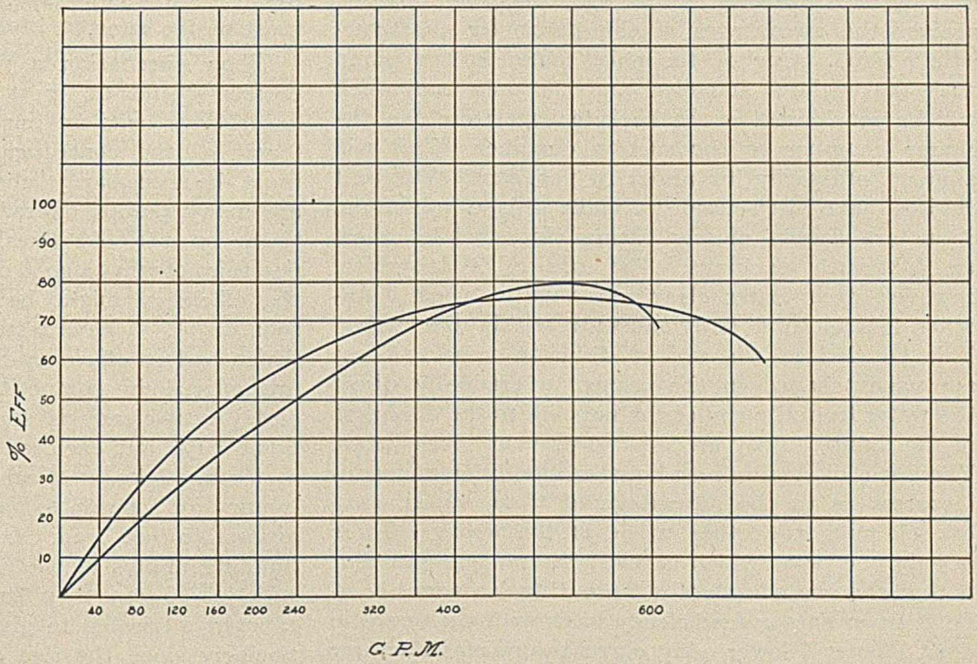
There are various difficulties which occur in the operation of centrifugals, and manufacturers have been working to overcome them. The first trouble of any importance, after the centrifugal was designed according to scientific principles, was end thrust. This was overcome hydraulically by various methods, but there is almost always some unbalanced thrust that will cause trouble if it is not cared for by mechanical means. The thing next in importance is low efficiency. Every effort in both design and construction had been given to create pumps which will deliver the highest possible amount of energy compared to that put in. Large strides have been made, and new ideas are described with great claims for them. There has also been simplification of parts, so that pumps can be built as cheaply as possible. Before taking these up more in detail, I shall recall a few of the principles which govern the design of the centrifugal.

In the first place, I would like to point out that formulas have been worked out for almost every part of every kind of pump. As with the water turbine, the design of the water passages, the shape of the vanes and the peripheral speed of the impeller have to be fixed for a definite amount of liquid against a definite head. If this amount of water is changed in any way whatever, the efficiency will drop; the alteration of the head will also change all of the dimensions. For this reason many manufacturers work out from operating pumps a set of charts which they follow, and the result is that the pump they deliver is not perhaps according to the best theories which have been formulated, but will meet conditions which the other pump will not. Even at the present time, if one wants a very flexible pump in regard to capacity and head, the manufacturers will not guarantee efficiencies very closely. One may work out on the drafting table the exact shape of the water channel, for instance, and any slight error made in the pattern shop, in the foundry or in the machine shop will alter the desired fine point so much that it will be completely lost. After the little alteration is made, and even worked up to the finished pump, a slight change, such as the pressure of the gland on the packing will more than offset the advantage gained. For this reason, we may aim more to accomplish what is wanted in the adaptability of the pump than to gain a small increase in efficiency.



The size of the pump is determined by the amount of liquid and the speed at which it is to be discharged. Usually a speed of 10 to 12 feet per second is used. It is then simple to find the pipe diameter. Secondly, we have to determine the head against which the pump is to discharge. This total head is made up of several different parts—pressure, suction, friction, velocity and orifice heads. If the inlet and outlet of the pump are the same, the orifice and velocity heads are measured as the suction head. The total head then becomes the sum of the pressure, suction and friction heads. To better understand how to adapt a pump to any total head, let us consider what speed must be used to force water up into a very high standpipe. If the water has reached a standstill and nothing is being discharged, the speed of the impeller must be such as to hold the water against that pressure. It can be compared to a falling body, and the velocity of the periphery of the impeller will be the same as that of a falling body, falling from that height in a vacuum. We can easily calculate that speed from the law of falling bodies, $V = \sqrt{2gh}$. For the pressure which the pump can maintain with no discharge this law will be exact, but when the pump delivers water, there are a large number of other factors to be considered. The first factor is the angle between the vane in the impeller and the tangent at the rim. In a general way the larger the angle, the less the pressure will drop with an increased delivery and constant speed and *vice versa*. If the angle mentioned above is small, the pressure will drop; if it is about 30°, it will be almost constant; if 45°, it will rise slightly at first and then drop with increased delivery and if radial or greater than 90°, it will rise almost its entire length. For ordinary work, the different manufacturers have a set of curves which show exactly what each form of impeller will do. These are obtained by testing every pump they make and tabulating the results accordingly. For the working pressure the formula then becomes $V = n\sqrt{2gh}$, where n is dependent upon the angle between the vane and the tangent to the circle. The amount discharged will also depend upon the width of the slot. If we draw a parallelogram with the base equal to the peripheral velocity, the angle between the base and the side that of the tangent of the vane and the tangent of the circle and the altitude equal to the velocity of the water from the impeller, then the diagonal drawn from the angle of discharge will be the velocity head of the water under those conditions. Theoretically the cross-section area of the slot at the rim should be the same as the suction opening at the hub, but many manufacturers make it 85 per cent. of that area, increasing the speed of the water slightly as it passes through the impeller. From this, for a given discharge rate of flow, it is seen that the width of the slot depends upon the diameter of the impeller, which in turn depends upon the speed at the periphery and the working head. Many different kinds of motive powers are used and to meet the speeds of these the pump has to be designed with different impeller diameters so that the proper peripheral speed may be obtained according to the head and vane of the impeller. Since the angle of the vane controls the value of n in the formula $V = n\sqrt{2gh}$ many designers keep that angle the same at all diameters, so that the diameter of an impeller can be changed by simply turning it down on a lathe. A spiral having that property is a logarithmic spiral having the equation Log $\rho = b\theta$ or $\rho = a\varepsilon^{b\theta}$. It will also be noticed from the law of falling bodies that the head varies as the square of the speed. In other words, if we want to double the head we multiply the speed by 1.414. Also, if we increase the speed at the rim, we increase the speed of the water through the impeller, so that the pump will discharge a much larger quantity of water. The increased amount of water which the pump will throw will depend upon the size of the suction opening and the internal friction of the impeller itself. This can be closely determined by using a constant for the impeller. This constant is equal to the quantity at any given speed, divided by the square root of the head. If then, we determine n in the formula $V = n\sqrt{2gh}$, where n is the ratio between the working head and the shut off head, and then apply the above formula $K = \frac{Q}{\sqrt{h}}$, we can easily determine the quantity which the pump will discharge at the higher speed.

Also, it is shown that at a given peripheral velocity a small impeller run fast is more economical than a large one run slowly, for the smaller impeller has much less surface, and although the friction increases with the speed it increases more rapidly with the larger surface. In the installation of the centrifugal pump, the quantity and the head for which the pump is designed should be adhered to as closely as possible. There will be a narrow range in which the efficiency of the pump will be the highest. Every effort is made to make that range as wide as possible, for under every-day working conditions, we cannot expect the pump which will pump only one quantity against one head to be satisfactory, and the larger the range under which a pump can be used, the better it will be commercially. Some of these difficulties can be overcome by the use of some kinds of motors but they will be considered later.



As stated before, one of the practical problems in the design of a centrifugal pump is taking care of the end thrust. There have been various ways of balancing this hydraulically, but the more important ones are those which were devised by Jaeger and by the Sulzer Bros. in Germany. With single stage pumps, the one devised by Jaeger is used where the pump has an enclosed impeller and but one suction. The idea consists in placing a running ring on the side of the impeller opposite the suction and connecting the chamber so made with the interior of the impeller by suitably placed holes. This and other devices to overcome the end thrust of single suction pumps is very satisfactory as long as the pump does not wear beyond the point of adjustment. In double suction pumps the pressure is hydraulically equal. It is better, however, to place a small collar where it can take up inequalities. There are many little things within a centrifugal pump which might cause thrust, and some of these are utilized by different manufacturers to balance the axial pressures, but the amount of thrust will change with wear and there are usually troubles from this source. Besides the single suction feature, thrusts will be caused by ribs inside the casing. If there is need for repair of a brace inside the casing, the rib or lug will cause an unequal flow on one side of the impeller, and thrust will result. Another cause is that in the casting of an impeller the core is usually made in two pieces, and if these are not placed properly the vane will have a diagonal slant which will cause unequal discharge from the rim. Also there will be an oblique discharge from an impeller, the one side of which is shorter than the other side, or, if an impeller has a piece knocked out of one side, it must be filled in very accurately and carefully, so that there is neither a lug on the side of the impeller, nor an open place in the rim. The best way to remedy this difficulty is to put a ring entirely around the circle, with the piece to fill the opening attached to it. A large number of manufacturers consider it an advantage which increases the efficiency of a pump to use diffusion vanes. If diffusion vanes placed in the casing are not exactly in line with the slot in the impeller, there will be thrust, so that if any are operating a pump having diffusion vanes and, after it has been assembled, the bearings begin to run hot, it might be from this cause. There is another way of balancing a single suction impeller, and that is by using a disc attached to the shaft and so located that the pressure of the discharge is on one side, and either atmospheric or suction pressure on the opposite side. The criticism of this type is that the wearing joint will increase the leakage, and the thrust will not then be balanced.

To increase the efficiency, I have mentioned the enclosed impeller. The angle of the vane will influence the efficiency for the reason that it will increase or decrease the internal friction by changing the length and cross-section of the channel. Also, the smaller the angle the lower is the working pressure at the same peripheral speed. This necessitates running an impeller with the small angle much faster than one with the larger to obtain the same working head. This creates more friction and a lower efficiency. Since the angle of the vane is determined by the characteristic desired, this loss of efficiency must be balanced against the advantages of the particular characteristic needed. One of the chief losses in the pump with the enclosed impeller, and the only one which will be considered, is the back leakage from the discharge chamber to the suction chamber. This will amount ordinarily to about 5 per cent. Different devices have been used to make this a minimum. Some are simply closely fitting rings, while others are labyrinth packings. The use of a labyrinth, however, necessitates clear water with no grit. Another loss is from eddy currents within the casing. This has led to the use of diffusion vanes. These are vanes shaped in the casing to gradually direct the water from the rim of the impeller to the discharge of the pump. They are used to prevent shock losses. There is a discussion now between the different manufacturers as to the advantage of these vanes, each one claiming the other to be in the wrong. There is only one point which is really interesting, and that is that the one who does not use diffusion vanes competes upon an equal efficiency basis with the one who does. To still lower eddy currents, one manufacturer divides the casing opposite a radial discharge with a vane so arranged that the water must take the shorter route to the discharge opening. This pump seems to show about the same efficiencies as the others. There has been introduced recently a pump in which the diffusion vanes are fixed in a ring that can turn free from the hub of the impeller. The shape of the vanes in this ring are of course different from those in the stationary vane, and it is claimed that this revolving vane increases the efficiency 25 per cent.

There is always the aim to use a more simple design to decrease the price. When a manufacturer has to meet competition, he will frequently offer a pump which is simpler, and for which the same efficiency is guaranteed. It will be seen on close examination that there is a lack of one of the chief features desired—either accessibility, ruggedness of design, or some such point. The pump will have but one bearing, and will depend either upon a gland for a bearing or upon a rigid coupling to the motor shaft, and use the motor bearings. Another scheme is to place the armature of the motor and the impeller of the pump on the same shaft. One manufacturer has brought out a line of both horizontally and vertically split pumps, so that they can be assembled in single or multiple stages to suit the condition. The use of the vertically split shell seems to me to be a poor design for the reason that just where one needs wearing qualities, there is a joint and packing. Also, the distance at the running joint depends somewhat on the packing. With the single piece volute or the horizontally split shell, the running joint is always fixed when the rings are made, and the distance between them is a minimum. I might state here that in replacing a sheet packing at any time in a pump, the new packing should be exactly the same thickness as the original packing, because in machining the case, the work is usually done with the packing in the joint, and in order to have the casing the correct shape, the thickness of the packing must be the same.

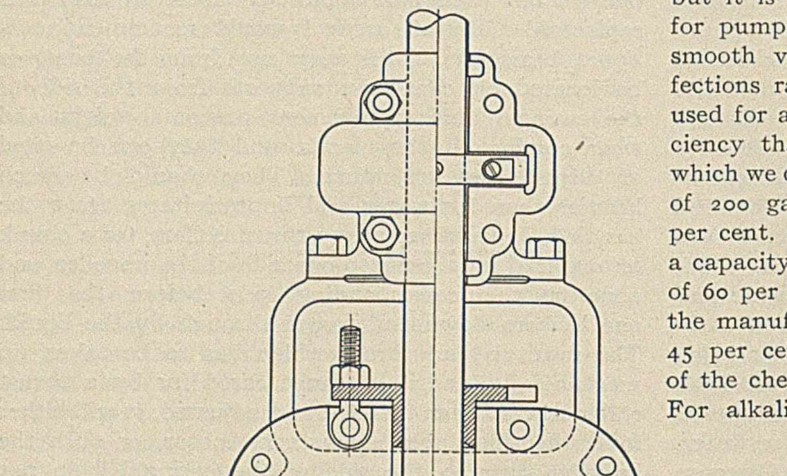
When purchasing a pump from the dealers, the details should be most carefully examined. There has always been an impression, created by the first forms of the centrifugal, that this type of pump must be necessarily cheap. For this reason there are many pumps offered to-day which are built entirely on the old lines. These pumps cost about one-third of what a good centrifugal costs, and although the efficiency might be quite high at the start, it soon drops. I have tested new open impeller pumps, which had an efficiency of 18 per cent. These pumps are offered in competition with the better grade, and the efficiency is stated as high or even higher. Some have put enclosed impellers in old casings and so forth. I know of an instance where a firm made inquiry for a pump to handle 5000 gallons per minute against 50 foot head. One of the firms who had been building pumps of the old type had advertised very widely a pump they had just designed and it was thought advisable to give them a chance, more particularly since the size of the pump advertised was the size needed. They had mentioned an efficiency of 70 per cent., and other features known to be of advantage. When the proposal was received, it was the same old design, with the open impeller, the glands for bearings and so forth, which they guaranteed to have an efficiency of 70 per cent. They were asked why they had gone to the trouble of designing and advertising the other pump when the old style was guaranteed at the same efficiency, etc. No answer was ever received. Many of the dealers in the old line advertise the same as the more modern manufacturers and when a purchaser sees that the machine is not up to the guarantee, they offer every possible excuse. One of these pumps failed when tried on the work for which it was intended. The pump dealer said that it was the turbine, and the turbine dealer said it was the pump. I have seen them use motors out of all proportion to the efficiency guaranteed. Recently in one of the most modern plants in Detroit, I saw one of these pumps with a 40 horsepower motor doing 14 horsepower work, and the motor was running so hot that the hands could not be held on the frame. The pump was guaranteed higher than even the most modern pumps can reach, but the motor pulled the load and the outfit was thought satisfactory. The longer an enclosed impeller pump is operated the smoother it becomes and the higher is the efficiency, provided that the running rings are not unduly worn. These can be replaced at very slight cost at any time, and the efficiency will be higher than when the pump was new.

In using one of these pumps for chemical problems, there are many things to consider besides the efficiency, yet this should be kept as high as possible. The pump must meet the conditions, and when the chemical engineer has to pump liquids of different densities from different tanks, at different levels through suction lines of different lengths to tanks similarly situated, the head is by nó means constant, the gallonage varies through wide limits, the power required varies sometimes 300 per cent., and the dealer says it cannot be done. Other manufacturers think they can meet the problem, but it is too wide and varied for them to understand, and the pump frequently fails. A pump was purchased by the writer for moving a heavy viscous liquid full of sediment from one tank to another, a firm having agreed to build a special pump at twice the regular price of one made for water. It came and was installed under protest because many parts seemed too light, the slot too narrow, etc. The builder said to instal, and if it did not meet the conditions they would repair. The pump lasted three weeks. The glands were torn out, the sleeves on the shaft were scored and cracked, the liquid had wormed its way into the joint between the impeller and the shaft causing the runner to wobble. It was torn beyond repair, and the running rings were useless. The firm rebuilt the pump, and it is now pumping water. We designed and built our own pump after that trial. In the design of that pump, we eliminated everything we could and built a very heavy design throughout.

In a pump for chemical use where the upkeep is considerable it seems to me that simplicity should be the first consideration. Although small clearances might increase the efficiency slightly, they should be avoided except in the running rings and these should be made easily replaceable. Avoid a labyrinth packing, because it has too close clearances, and will wear excessively. Use single stage pumps, using two rather than one double stage. In this way the use of diffusion vanes are avoided, and narrow passages are not needed except in the impeller. At the exit of the impeller, do not make a narrow running joint, but leave it more like a box. The efficiency may not be as high, but you can then alter the size of the impeller at will, and there are only smooth surfaces within the casing. Secondly, the chemist's pump must be easily accessible. For this reason, we built a horizontally split machine. These are made by several manufacturers, and are very easily opened to clean out a choked impeller, or to renew running rings. Another change which we made on the pump was the separation of the suction opening from the volute. On most of the pumps of this type, unless they are extremely large, the entire volute and suction connections are made in two pieces, but for accessibility and renewals, we separated the casing into seven pieces, the upper half, and the lower half, of the volute, two pieces divided horizontally on each side, and the two suction inlets were joined by a Y pipe. The running rings should be as plain as possible, because all edges will wear. If a passage with an angle in it can be used it will be well to put one in, but each part should be made so that it is replaceable. In all cases I would recommend outboard bearings. These may rise from the base, or be located on cantilever supports from the side of the casing. This arrangement prevents weight and wear coming on the glands, and they can be oiled or adjusted at any time. They should be much heavier than for water and if precipitates are to be handled, I would use heavy thrust collars, for a chunk of material may get into one side of the impeller and none in the corresponding side before the first one is worn down and forced through by the liquid. The result is end thrust which has to be taken up mechanically, and if it is not cared for by a thrust collar where it can be oiled and adjusted, it will either force the shaft over against the motor, or push the impeller over to the side of the casing. I do not think that a marine thrust bearing is necessary, but a thrust collar will not be useless. Frequently, rivet heads, bolts or trash will get into the chemist's pump from open tanks and these will disturb the hydraulic balance of the pump. In pumping precipitates, a screen inserted in the suction pipe increases the suction head on the pump, and sometimes will plug with the precipitate. Before inserting such a screen, the local conditions should be very carefully considered.

The pump for chemical purposes should be built very heavy and rugged. The casing should be made very thick. As a general rule, it seems to me to be much better to build the casing very heavy than to use a thin casing and line it. In pumping alkalis and some acids, the casing can be of the same material as the liner, and the outside skin of the casting will stand more than most materials of which a liner can be made. There is good reason, that of electrolysis, why a lining of a different material should not be used in a chemist's pump. This will be emphasized later. This also applies to sleeves on shafts. It is better it seems to me to replace a shaft, if it is of not too expensive a material, than to use a sleeve. There is always corrosion at the glands, and where there might be electrolysis a sleeve does more harm than good. With the heavy casing should be used heavy flanges. These will stand any pressure which might be put on them from outside. If a pump plugs with a precipitate, the easiest way to clean it out is to put high pressure water on the pump and push the plug out or dissolve it. The heavy casing and flanges will not give trouble under these conditions.

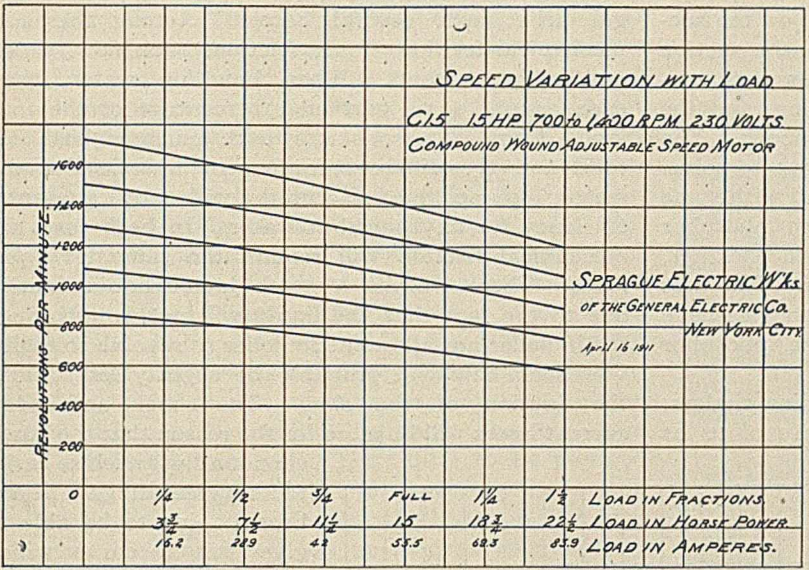
I have seen thin pumps break when this was being done. They will also stand much more water hammer, which sometimes occurs when a pump is pushing the water to the top of a tower or standpipe and is suddenly stopped. I have mentioned the shaft and glands. These should be built heavier than for water and it is better to so shape the casing at the side that it protrudes inwardly to the impeller, because this method keeps the liquid or precipitate from the shaft. No sleeve need be used with this construction, and the casing takes the wear. I have seen these inwardly projecting pieces chew down over one-fourth of an inch in eighteen months. We simply machined them back a short distance, and kept them in service. Another point about the gland piece itself is the fact that when there is a liquid pressure on the gland, there might be a slight leakage from the joint where the shaft enters it. It is well to make the gland thick, and put a channel in the outside of the gland piece so that there will be no spray radially from that point. If there is, it will be caught in this channel and from there to suitable receivers. The impeller will wear away faster than any other part. This is due to various causes, and the only way which will really give the best service, is to build it very thick and heavy. For water, the usual thickness is about $^3/_{16}$ inch, but I do not think $^3/_8$ or $^1/_2$ inch too much. I have seen cast iron impellers of that thickness wear out in 4 months so that the thinner impeller would be almost useless. This means special patterns for the manufacturer of water pumps, but it more than pays. In placing the impeller on the shaft, be sure that the liquor will not be able to get at either the key or the shaft. If it does it might cause the impeller to wobble, with results that are obvious. The surfaces should be as smooth as possible, but it is not necessary to make them as smooth as for pumping water. Most solutions will wear them smooth very quickly, and will destroy any imperfections rapidly, so that an impeller which has been used for a month will show a very much higher efficiency than the new one. I have seen an impeller which we did not take the time to polish have a capacity of 200 gallons per minute and an efficiency of 25 per cent. Four months later this same impeller had a capacity of 300 gallons per minute and an efficiency of 60 per cent. The efficiency usually guaranteed by the manufacturers of this type of a pump is between 45 per cent. and 58 per cent. In the construction of the chemist's pump various materials can be used. For alkalis an all-iron pump meets the condition very well. When the alkalis are full of a precipitate a harder metal must be used. The running rings may be made of monel metal, or nickel steel.



For some solutions, we can build the pump of bronze, monel metal, hard lead, or stoneware. I do not like stoneware pumps, as the strength of the material is very low, and because of this, slow speed must be used. This means that the efficiency is low, and as I have never seen a stoneware enclosed impeller, the efficiency will be very low indeed. I have never had a stoneware pump tested, but better made iron pumps took power out of all proportion to the work done. One of the problems which the chemist must always face is the speed of the impeller. With water, and most alkalis, the impeller can be made of monel metal and the rim speed can be most anything desired or practical, but in pumping acids, it must be very carefully examined. Many of the metals and alloys withstand acids for the reason that there is formed on the surface a skin of oxide or a salt, which adheres to the metal and protects it. When this is used in a reciprocating pump, the salt is hard enough to withstand the slow speed, but on the rim of an impeller it quickly erodes, and the impeller is dissolved very rapidly. Some alloys which will resist acid for years in tanks, etc., will dissolve in a few hours when made into an impeller. The only way out of the difficulty, is to either use some other form of pump, or to use several pumps in series, keeping the rim speed of the wheels slow enough to leave the protecting skin in place. The multiple stage pump for chemical use has too many complicated parts in one casing.

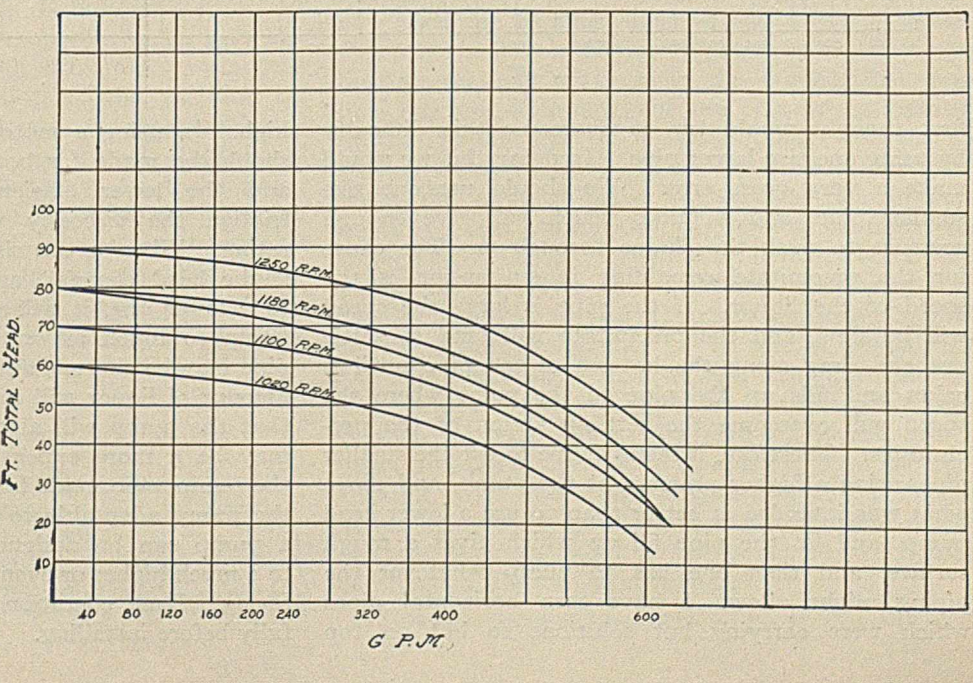
Several single stage pumps in series it seems to me are better, for then trouble can be exactly located and quickly eliminated.

Corrosion also might be from the use of different metals, causing electrolysis. With a rapidly moving surface, which is always clean and bright, electromotive forces will do far more than where sediment is allowed to collect. I have seen monel metal withstand alkali solution for months, even at high speed, and I have seen a monel metal running ring worn out in a month, where a bronze ring was placed next to it. Many times, two metals such as cast iron and mild steel will have an electromotive force between them sufficient to cause trouble, and a peculiar fact is that one may be positive in a dilute solution and the opposite in a more concentrated solution. This is probably due to the fact that the change in the dissociation of impurities changes the real electrolyte. Sometimes it is possible, by placing in the suction line a heavy thick pipe made of a metal which is electropositive to the material of the pump, to plate and keep plated the inside of the pump, so that both the pump and the pipe will last for a long time, where the pump alone would quickly corrode. This makes the entire outfit practically of one metal, all the different electro-negative parts become polarized, and the corrosion ceases.



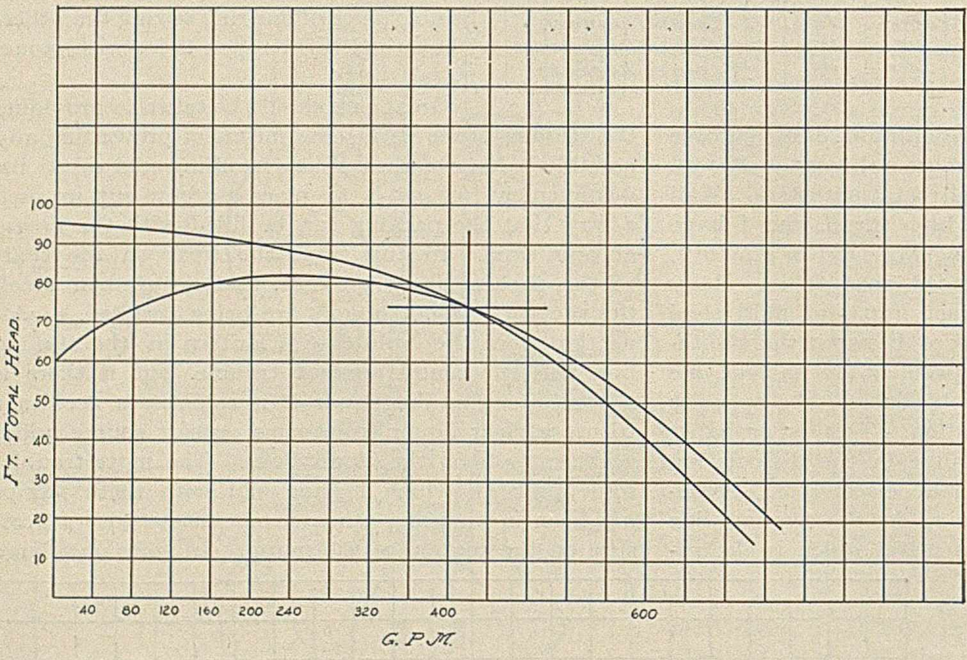
When handling precipitates, impellers erode very rapidly. As shown before, the capacity and the efficiency increases, and this will continue until the wheel will drop into three pieces, the hub and the two sides. As it wears, a peculiar cutting action appears on the under side of the impeller vane. This is more pronounced than on the upper side, and it cuts away the outer edges faster than the center leaving a ridge. Not only does the slot become broader, but the outside of the shroud also wears away, about in proportion to the distance from the hub. The wearing is dependent also upon the hardness of the material from which it is made. I have not made scleroscope tests, but government bronze in alkali solutions lasts longer than cast iron, monel will last longer than government bronze, and nickel steel the longest of any tried. These were pumping approximately the same material, containing 60 per cent. by volume of precipitated salts. This property of hardness applies to all parts of the pumps, the running rings even more than the impeller. In using metals for the rings, however, the selection must be made so that there will be no chance of one ring seizing the other. I have had this happen twice with monel metal.

Great care should be taken in providing the stuffing boxes with some means of preventing any possible leakage of air. When handling cold solutions, a convenient means is to place a grease cup in such a way that the packing can be filled with the grease at any time. In this way, the wear on the shaft at the packing is very slight, and no air can break the suction. If hot liquors are being handled, a connection from the volute to a lantern in the stuffing box will effectually prevent trouble, but if there is a precipitate in the liquor it is sometimes necessary to use a clear liquor from some outside source under pressure to keep the gland tight. The most troublesome problem which I have had with these pumps has been in pumping a heavy precipitate with a pressure on the suction of the pump. In spite of a large



stream running into the stuffing box from an outside source, the precipitate will force its way into the packing and cut it into pieces very quickly. I have seen a $^3/_8$-inch packing, 6 rings deep, cut to pieces in one hour, by salt getting into it. In pumping milk of lime, two stuffing boxes had to be repacked twice a day because there was a pressure on the suction of the pump. I inserted a plate in the suction line of the pump, which reduced the pressure to one-inch vacuum, while the pump was running, and the box did not have to be packed for a month. The question of packing has been a difficult one to solve. I have used asbestos, which is usually filled with some cotton. I have also tried asbestos with phosphor bronze wire, and various kinds of metallic packings, but all seem to cut the shafts quickly. The best shafts I have used have been of monel, although I have tried cold rolled steel, government bronze, phosphor bronze and tobin.

There is one point to be made in handling sludges. They are naturally hard to pump. Many of us at first thought would try to overcome this difficulty by using one size larger pipe. In doing this we would make a very gross error. We should use one size smaller pipe, and a pump which will give enough pressure to push the sludge through it. The cause for the precipitate remaining in suspension is the speed of the liquor. If the pipe is large the speed will be slow, and the precipitate will tend to settle out and drag along the bottom of the pipe until it cakes and fills up the pipe to the point where the speed will overcome the settling action of the precipitates. Therefore, it seems to me to use the smaller pipe, using a higher pressure at the pump, and move what was intended is better than to use a lower head pump, and let the pipe fill up which gives a rough surface, and then one has to pump whatever the piping might allow. I have seen horizontal pipes which were carrying hot solutions so hot on top that the hand could not remain on them at all, but comparatively cold on the bottom.



The chemical engineer has to contend with a variable viscosity. This is of far more importance when using a centrifugal pump than in using a reciprocating or rotary device. The mechanical losses in the centrifugal arise from several causes. Among these are mechanical friction, liquid friction, back flow, shock, and eddy currents. When handling water, these each assume some particular percentage of the total loss. A more viscous substance changes both the total and the different component losses. For this reason, pump manufacturers will not guarantee efficiency for anything but water. In both cases the mechanical friction will remain the same for equal loads. There will be a much larger liquid friction due to the fact that the liquid will not flow through the impeller nor allow the impeller to revolve so easily. The back flow will probably be slightly less due to the friction of the slot. The shock and eddy current losses will be more for the reason that the liquid cannot adjust itself so easily to its surroundings. I have been hoping to be able to give you a curve which would show the relative efficiencies of the pump with which I have been working compared to the relative viscosities. Owing to the trouble of measuring the amount pumped and the necessary alterations to accomplish this, I have not been able to work the data out at this time. We may use larger piping and slower speeds if the viscous solutions contain no sediment. The impeller should also be built to deliver at a very much slower speed than for water. In this way, the efficiency might be kept up reasonably high. In using a motor for this purpose, allowance should be made for both the higher specific gravity and the lower efficiency. When calculating pipe friction the viscosity will greatly alter the water rating. When a centrifugal is pumping any liquid, if the head changes, as in changing from one tank to a lower one, it will not affect the working of the pump so much as one might think. Although the pipe may be shorter, and the tank lower, an increased amount of liquor will raise the pipe friction so much that the pump will alter its load but slightly. This may be a more expensive way of pumping than if the pump were made for the lower head but it makes the pump adaptable to both conditions. Frequently a pump can be designed to pump a small amount to a much higher or even a lower head than the normal rating. Each condition must be studied most carefully before installing.

There has been developed a novel pump for the use of chemical engineers which has an application where other machines fail. The most serious difficulty in handling acids is the material of which the pump can be made. A line of hard lead pumps designed like those of 20 years ago, has been on the market for a long time. They cut out very quickly, and most of the trouble is at the gland where the sleeves quickly erode so that the steel shaft is exposed. This pump overcomes all such troubles for the reason that it has no gland, nor packing, and can be made on the most modern lines. The impeller can be either enclosed or open, and it can be built for heads up to even 75 or 80 feet. The shaft is vertical, very heavy and covered with a hard lead sleeve. It is supported from two bearings placed from 3 feet to 6 feet apart according to conditions. The impeller is at the lower end of the shaft, overhung perhaps 6 feet. Around the impeller, is a suitable casing with discharge connections. The suction opening to the casing is the novel feature. It extends upward like an open pipe for about four feet. The liquid to be pumped is simply fed into this open pipe, either at the top, or in the side. The surface of the liquid in this pipe assumes its own form, but as long as there is any in this receiver it will be forced according to the speed and construction of the pump. They can be built of any capacity or head desired.

In closing, I want to mention an arrangement of a centrifugal pump with direct current electric motors. We all know how a series wound motor will operate under varying load. It changes its speed running faster as the load decreases. If in pumping sludges, we use a pump with a drooping characteristic and then use a highly overcompounded motor, the pitch of the characteristic can be made very steep. The operation of a pump under these conditions is such that a decrease in quantity discharged decreases the load on the motor, which instantly speeds up, creating more pressure and removing a plug almost before it has formed. This same idea could be applied to a pump which has a rounded characteristic. As the pressure tends to drop with the quantity on very low discharge, the horsepower will also drop, causing the motor to speed up. The result is that the shut off speed of the motor is higher than the working speed, and the shut off pressure is accordingly higher. If we have to pump into a tower, where the starting pressure must be higher than the operating pressure, this motor will assist in obtaining that result without using the impeller with the longer channels. Many times also, an adjustable speed motor will help us to obtain that flexibility of the steam pump, with the advantages of the centrifugal, with a speed variation of less than 40 per cent.

NEW FORMS OF GAS ANALYSIS APPARATUS.[1]

By G. A. Burrell.

Received January 2, 1912.

The gas analysis apparatus here presented were assembled by the author for the conduction of work having to do with the examination of mine and natural gases. The points of novelty involved lie in the entire assemblages. The author took what he considered some of the best features common to some other types of apparatus and assembled them in the apparatus shown.

This particular apparatus is useful for a large class of analyses and quite precise work can be performed with it.

The burette has a capacity of 100 cc. and is graduated in 0.10 cc. Readings can be made to 0.05 cc. The compensating attachment is similar to Hempel's adaptation of Petterson's principle. Mercury is used both in the burette, combustion pipette and manometer tube *j*. The gas sample is drawn into the burette through the 3-way stopcock *g*. The burette is graduated from *g* down. Pipette *a* contains caustic potash solution for absorbing carbon dioxide; *b* contains fuming sulfuric acid for absorbing unsaturated hydrocarbons; *c* contains alkaline pyrogallate solution for absorbing oxygen. These three pipettes contain glass tubes (not shown) for increasing the absorption surface of the solutions as in other Orsat pipettes; *d* and *e* contain cuprous chloride solution for absorbing carbon monoxide. The pipettes *d* and *e* are similar to the pipettes devised by J. E. Babb[1] and used by him for absorbing carbon monoxide from a gas mixture by means of cuprous chloride solution. A side view of the pipette is shown at *m*. The gas mixture as it enters the pipette passes down through the central tube extending into the pipette. It then bubbles up through the solution and lodges in the top of the pipette, forcing the cuprous chloride solution into the reservoir bulb of the pipette. To draw the gas back from the pipette, the stopcock is turned as shown at *m*. Two pipettes of this character when filled with cuprous chloride solution are sufficient, when one of the solutions is kept quite fresh, for the removal of carbon monoxide from mixtures, even when the former is present in great concentration, and for the analyses of any of the industrial gases now used for heating, lighting and power purposes; *f* is the slow-combustion pipette. The slow-combustion method of burning the combustible gases in a mixture, admits of the use of a larger quantity of the residual gas for analysis, than when the explosion method is used. This is especially important when the mixture being analyzed is rich in combustible gases, as natural gas, which contains, not infrequently, 99% of paraffin hydrocarbons. Residual gas left after the absorbable constituents are removed and which is rich in combustible gases is handled in the following manner: The gas is passed into the slow-combustion pipette, and the platinum wire therein heated to a white heat; sufficient oxygen is then introduced into the pipette, at the rate of 10 or 20 cc. per minute, to completely burn the combustible gas. The slow-combustion method possesses a further advantage in that hydrogen or electrolytic gas does not have to be added to a non-explosive mixture for the combustion.

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[1] Paper read before the Industrial Division of the American Chemical Society, 45th meeting, Washington, December, 1911. By permission of the Director of the U. S. Bureau of Mines.

[1] Engineers' Society of Western Pennsylvania, **20**, 421 (1904).

For a separate hydrogen determination, the palladium asbestos tube shown attached to *n* is inserted just above the slow-combustion pipette *f*. A small alcohol lamp mounted on a stand provides the necessary heat, about 100° C., for the combustion of the hydrogen.

The pipette *i* contains alkaline pyrogallate solution. Before beginning a series of analyses, air is introduced into this pipette and the oxygen removed. Before beginning a particular analysis, a few cc. of this nitrogen are drawn through the tube *p* into the burette and then discarded into the atmosphere to sweep out of the tube *p* oxygen or other gases left there from a previous analysis. This procedure in conjunction with the drawing of the gas sample into the burette through the 3-way stopcock *g* avoids the so-called capillary error introduced when the gas sample is drawn into the burette through the end of the capillary train, as in the ordinary Orsat apparatus. For less accurate work water can be used both in the burette and slow-combustion pipette.

In Fig. 2 is shown a portable apparatus of the type just described. The gas sample is taken into the burette through the 3-way stopcock *a*. Water is used both in the burette and slow-combustion pipette. Some accuracy is of course sacrificed by the use of water, but the apparatus was built for technical purposes, with the idea of utilizing the slow-combustion pipette for burning methane and hydrogen, and the Babb pipettes for the carbon monoxide determination. Some analysts, however, prefer the explosion pipette. Consequently it can be furnished if desired. The usual capillary error in an apparatus of this type is avoided by using the end pipette for the purposes already described and the drawing of the sample into the burette through the 3-way stopcock *a*. Duplicate determinations should agree within 10 or 15 per cent.

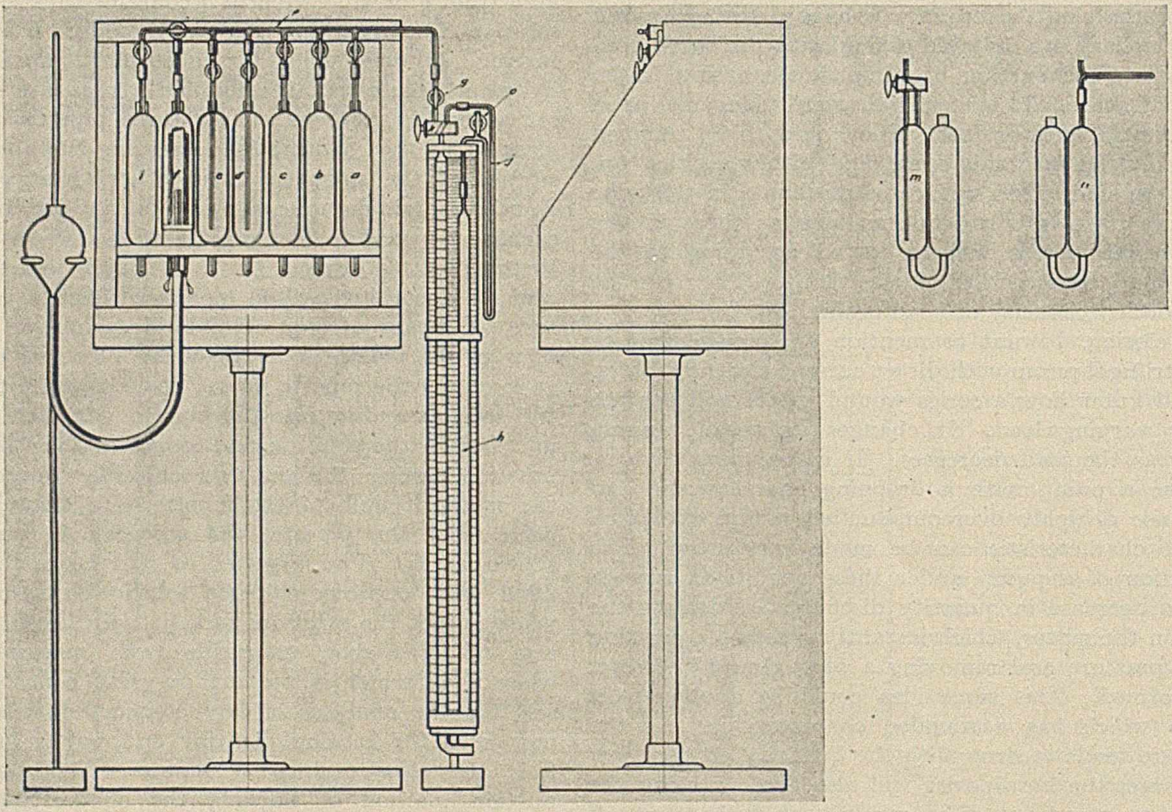

Fig. 1.—Laboratory form of apparatus for mixtures containing CO_2, O_2, C_2H_4, CO, H_2, CH_4, and N_2. Capacity of burette, 100 cc.; burette graduated in 0.1 cc.

APPARATUS FOR THE ANALYSES OF NATURAL GASES.

The apparatus shown in Fig. 3 is a modification of the apparatus shown in Fig. 1, and is used at the bureau laboratory in analyzing natural gases. Natural gases appear to consist of paraffin hydrocarbons with carbon dioxide and nitrogen present as impurities. Oxygen seems to be present in a sample only as a result of faulty sampling. Carbon monoxide, hydrogen and olefine hydrocarbons have not been found in mixtures thus far examined at the Bureau laboratory. The apparatus shown consists of the pipette *a* for removing carbon dioxide, the pipette *b* for removing oxygen, the slow-combustion pipette *c* and the nitrogen pipette *d*. Mercury is used in the burette and the slow-combustion pipette; 30 to 50 cc. of the residual gas left after the absorbable constituents have been removed can be used for the combustion analysis.

MINE AIR APPARATUS.

The apparatus shown in Fig. 4 is a modification of the apparatus designed by J. S. Haldane[1] for the analysis of mine air. The burette has a capacity of 21 cc. and is divided into the ungraduated bulbs at

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[1] "The Investigation of Mine Air," by Sir Clement Le Neve Foster and J. S. Haldane, 1905, p. 101.

the top having a capacity of 15 cc. and the stem graduated in 0.01 cc. and having a capacity of 6 cc. The pipette *a* contains caustic potash solution for the removal of carbon dioxide, and the pipette *c* alkaline pyrogallate solution for the removal of oxygen; *b* is the slow-combustion pipette. Mercury is used both in the burette and slow-combustion pipette. Burette readings are made against the pressure of air confined in the compensating tube by bringing the caustic potash solution to the marks *m* and *n*. Carbon dioxide, methane, and oxygen can be determined with an accuracy of 0.02%. Duplicate determinations usually check within 0.01%. Carbon monoxide and hydrogen can be just as accurately calculated from the combustion data by determining the oxygen consumed in the combustion. The apparatus has also been used at the Bureau laboratories for an accurate analysis of the constituents present in flue gases. It can also be used for analytical work connected with other ventilation studies than those having to do with mines.

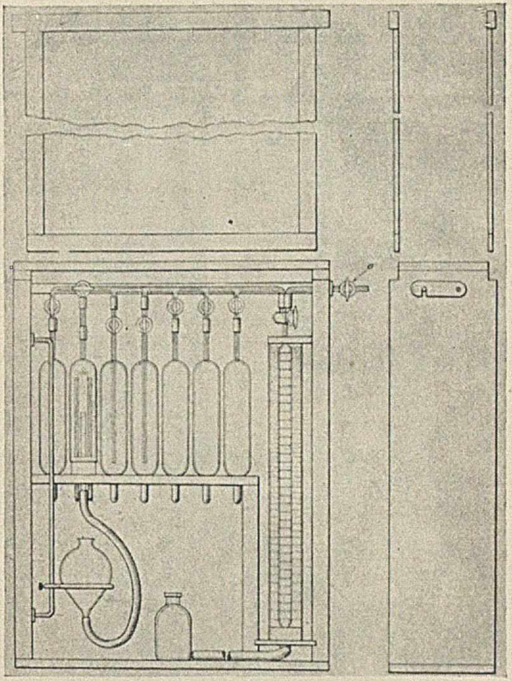
APPARATUS FOR METHANE DETERMINATION.

Fig. 5 shows an apparatus constructed for the exact determination of methane in mine air. At a few mines in this country and at many mines abroad, mine air samples are daily collected from different parts of the mine and examined as to their methane content. Winkler's titration method is generally adopted. In Winkler's[1] method the carbon dioxide formed by the combustion is absorbed in a standard solution of baryta water. The excess of baryta water is then determined by titration with a standard solution of oxalic acid. The scheme necessitates a preliminary determination of the carbon dioxide originally present in the mine air.

In the use of the apparatus shown in Fig. 5 the gas sample is drawn into the burette, measured by means of the manometer *b* and compensating tube *c* and then passed into the slow-combustion pipette *g*. The platinum spiral therein is electrically heated and allowed to remain so for three and one-half minutes. After burning, the pipette is allowed to cool and the gas then transferred back to the burette and the contraction in the volume due to the burning of the methane determined. This contraction in volume, when divided by 2 and calculated to a percentage basis, gives the methane originally present in the mine air. Mercury is used both in the burette and combustion pipette. Water is used in the manometer tube *b*. A determination can be made in less than 10 minutes with an accuracy of 0.01%. Methane is the combustible gas commonly found in coal mines, hence complications of the combustion data because of the presence of other combustible gases need not be greatly feared. Paraffin hydrocarbons higher than methane may be occasionally present, but if so usually only in traces.

PORTABLE FORM OF APPARATUS FOR DETERMINATION OF METHANE.

In Fig. 6 is shown portable apparatus similar in



ig. 2.—Portable apparatus for mixtures containing CO_2, O_2, C_2H_4, CO, H_2, CH_4, and N_2. Capacity of burette, 100 cc.; burette graduated in 0.2 cc.; water to be used in the burette and combustion pipette.

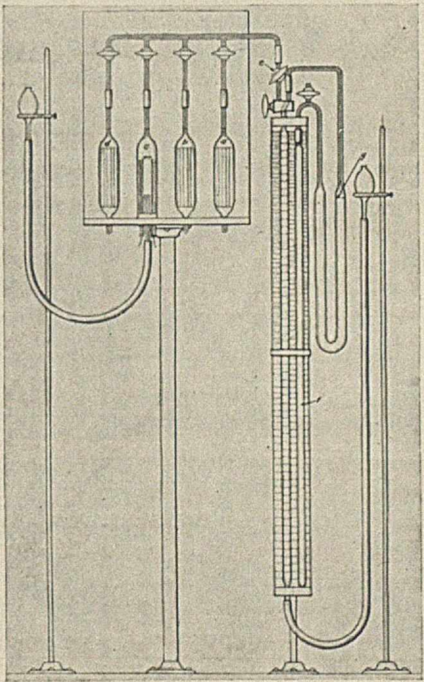


Fig. 3.—Laboratory form of apparatus for natural gas analysis. Capacity of burette, 100 cc.; burette graduated in 0.1 cc.

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[1] "Hand book of Technical Gas Analyses" by Clemens Winkler, 2nd English edition, translated by George Lunge, 1902, p. 156.

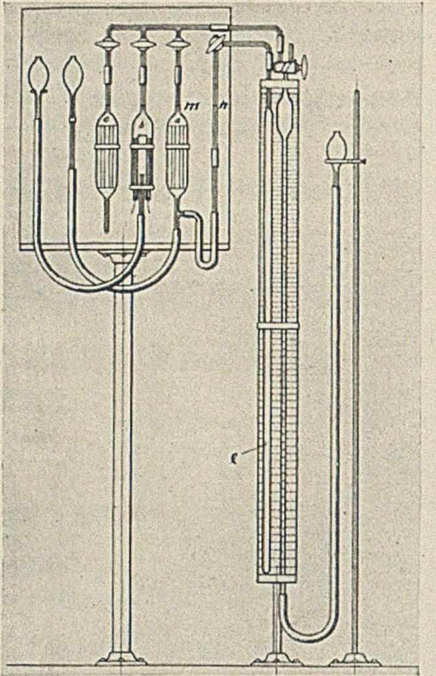

Fig. 4.—Laboratory form of apparatus for the exact analysis of mine air. Capacity of burette, 21 cc.; capacity of bulb of burette, 15 cc.; capacity of stem of burette, 6 cc.; stem graduated in 0.01 cc.

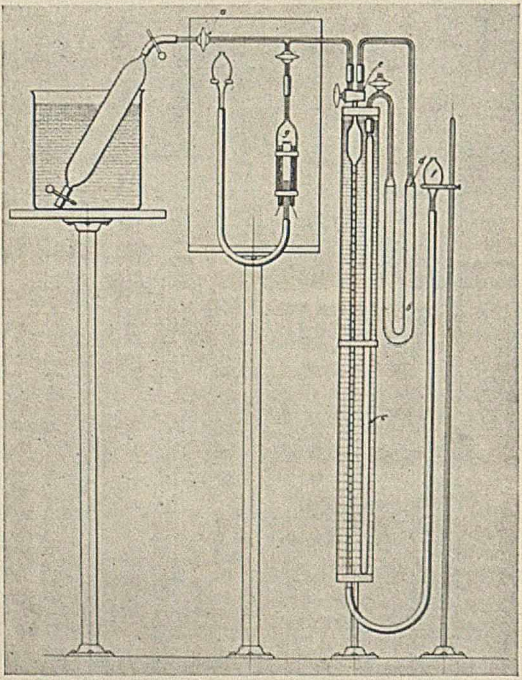

Fig. 5.—Laboratory form of apparatus for the exact determination of methane. Capacity of burette, 21 cc.; capacity of stem of burette, 6 cc.; capacity of bulb of burette, 15 cc.; stem of burette graduated in 0.01 cc.

construction to the one just described. A storage battery can be used to heat the platinum coil. A battery which will produce a current of 6 volts and 4 amperes is required.

In Fig. 7 is shown a portable apparatus which is a very simple form of gas analysis apparatus for the determination of methane. Water is used both in the burette and slow-combustion pipette. *b* is the slow-combustion pipette. It is accurate to 0.10%. This apparatus was devised for the purpose of making a quick determination of methane, for use by mining men who are not chemists. The sample is measured in the burette at atmospheric pressure and then passed into the slow-combustion pipette where the platinum coil is heated to a white heat for $3^1/_2$ minutes. After burning and cooling, the gas is transferred to the burette and the contraction in volume measured. This contraction is divided by 2 to find the methane.

PORTABLE FORM OF APPARATUS FOR THE DETERMINATION OF METHANE AND CARBON DIOXIDE.

In Fig. 8 is shown a portable form of apparatus for the accurate determination of carbon dioxide and methane in mine air. It is a modification of that shown in Fig. 4: *a* contains caustic potash solution, *b* is the slow-combustion pipette. Mercury is used both in the burette and slow combustion pipette.

In Fig. 9 is shown a portable form of apparatus for the accurate determination of carbon dioxide and oxygen in the air of public buildings, meeting-houses, school-houses, etc. It is meant to be used in connection with ventilation studies having to do with those places. *a* contains caustic potash solution and *b* alkaline pyrogallate solution. Mercury is used in the burette.

In Fig. 10 is shown a portable apparatus for the exact determination of carbon dioxide only: *a* is the caustic potash pipette. Mercury is used in the burette. Water is used in the manometer tube.

In Fig. 11 is shown a modified Orsat apparatus used by the author in the analyses of mine fire gases. Considerable aid may be rendered in subduing mine fires by analyzing samples of the atmosphere taken from behind stoppings, in order to determine whether the latter are sufficiently tight to exclude air, or whether, by reason of air in leakage, the embers are liable to fan into a blaze and make conditions worse. Analyses of the atmosphere are valuable to have during the entire period that the fire area is sealed, and before entrances are made to reopen the area.

The apparatus shown in Fig. 11 consists of the burette and the following pipettes: The caustic potash pipette *a*, the alkaline pyrogallate pipette *b*, the cuprous chloride pipette *c* and the slow-combustion pipette *d*. Water is used both in the burette and slow-combustion pipette. The pipettes *a*, *b*, and *c* contain glass tubes (not shown) for the purpose of increasing the absorption surface of the solutions. The apparatus is accurate to about 0.20%.

DETERMINATION OF SMALL AMOUNTS OF CARBON MONOXIDE.

The iodic acid method is used for the determination

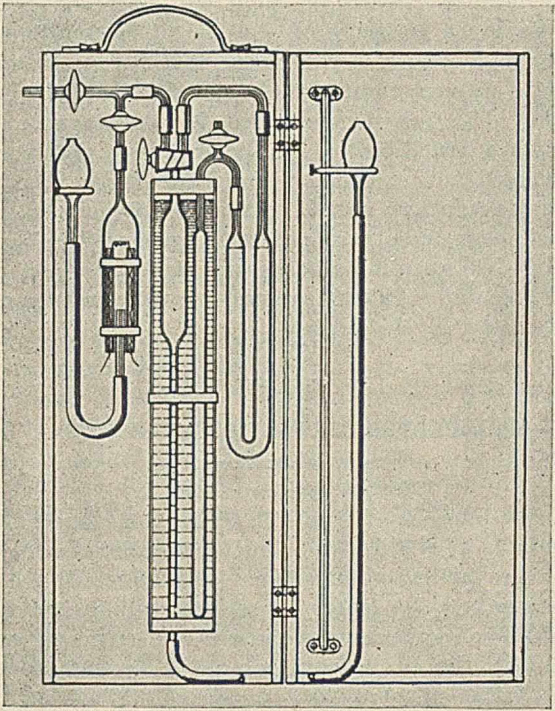

Fig. 6.—Portable gas analysis apparatus for the exact determination of methane. Capacity of burette, 20 cc.; capacity of bulb of burette, 17 cc.; capacity of stem of burette, 3 cc.; stem graduated in 0.01 cc.

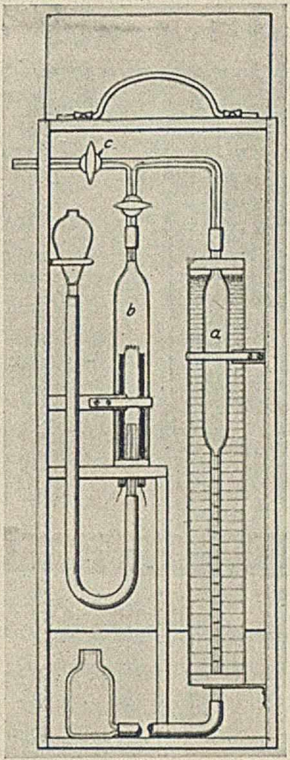

Fig. 7.—Portable apparatus for the determination of methane in mine air. Capacity of burette, 100 cc.; capacity of bulb of burette, 80 cc.; capacity of stem of burette, 20 cc.; stem graduated in 0.05 cc.

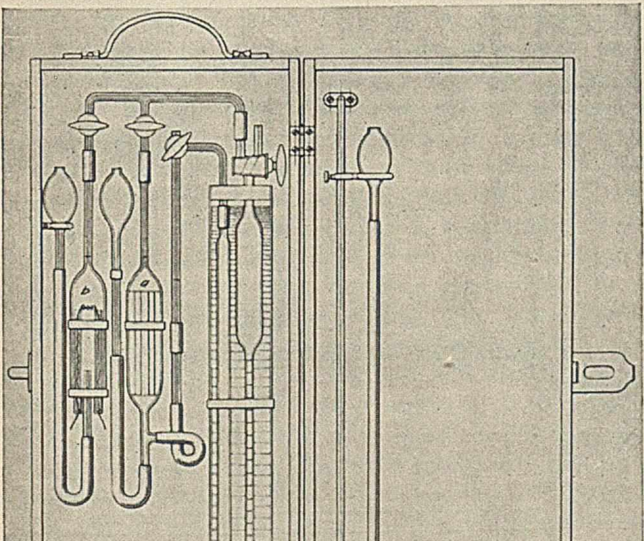

Fig. 8.—Portable gas analysis apparatus for the determination of carbon dioxide and methane. Capacity of burette, 20 cc.; capacity of bulb of burette, 17 cc.; capacity of stem of burette, 3 cc.; stem of burette graduated in 0.01 cc.

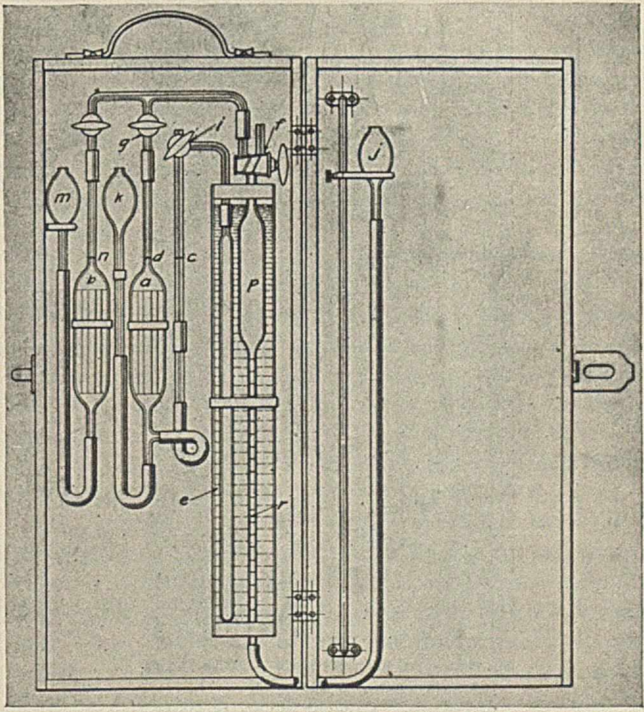

Fig. 9.—Portable apparatus for the determination of carbon dioxide and oxygen. Capacity of burette, 15 cc.; capacity of stem of burette, 3.5 cc.; capacity of bulb of burette, 11.5 cc.; stem graduated in 0.01 cc.

of very small quantities of carbon monoxide. The carbon dioxide formed by the reaction between the iodine pentoxide and the carbon monoxide is absorbed by a standard solution of baryta water and the excess of same titrated with standard oxalic acid solution.

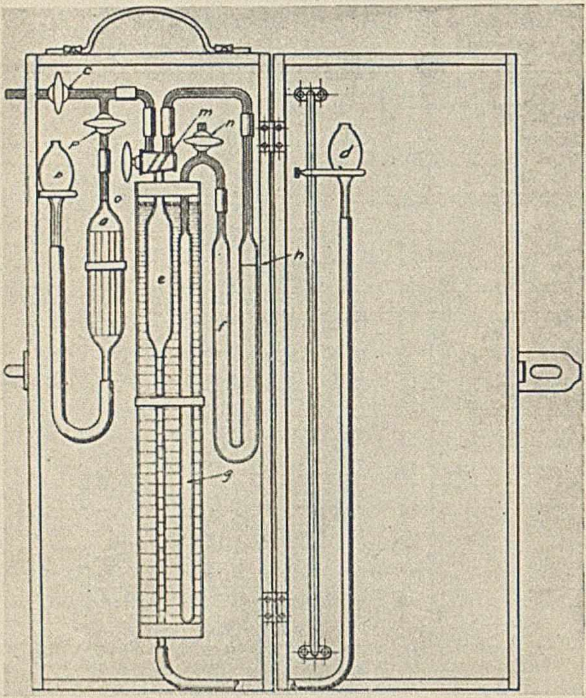

Fig. 10.—Portable apparatus for the determination of carbon dioxide in mine air. Capacity of burette, 20 cc.; capacity of stem of burette, 3 cc.; capacity of bulb of burette, 17 cc.; stem of burette graduated in 0.01 cc.

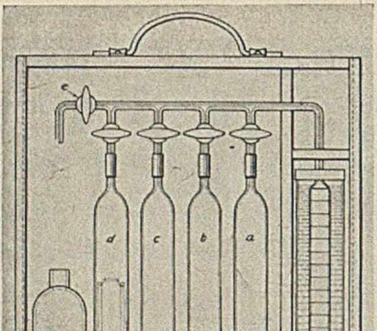

Fig. 11.—Portable apparatus used in fighting mine fires and exploring mines after explosions. Capacity of burette, 100 cc.; burette graduated in 0.1 cc.

The apparatus as used differs from other types in that an electrically wound jacket is used to heat the tube containing the iodine pentoxide and a special burette has been devised for holding the sample.

The burette consists of eight superimposed bulbs, each having a capacity of 100 cc. The constriction between each bulb is calibrated so that any number of bulbs up to eight can be used for holding the sample. The gas is measured in the burette by means of a level bottle, in the ordinary manner: a copper-constantine couple is used for registering the temperature, about 150° C., within the iodine pentoxide tube. These and other devices designed at the Bureau of Mines for examining gases will be fully described in a forthcoming bulletin prepared by the author and his associate, F. M. Seibert.

AN IMPROVED EXTRACTION APPARATUS.

By W. C. Blasdale.

Received December 18, 1911.

Many different forms of extraction apparatus, which make it possible to extract a number of samples with a low-boiling-point solvent simultaneously, have been described. A feature of all the more satisfactory forms of such apparatus is the use of electrical energy in heating the flasks containing the solvent at the desired rate. The apparatus here described utilizes electrical energy obtained from a 110-volt lighting circuit; it provides for five units, that is, for five separate heating plates and condensers. The general form of the rack used to support the extraction tubes and condensers is the same as that described by Hopkins (*J. Am. Chem. Soc.*, **21**, 645). It differs from the latter in that the energy of the current is changed into heat by passing through resistance wire instead of through incandescent lamps, the heat thus generated being imparted directly to the five iron plates upon which the flasks rest. It differs further from any of the forms with which the writer is familiar in that a condenser is attached directly to the frame of the apparatus, which condenser can be easily connected with any or all of the flasks while still in position on the heating plates, thus rendering it possible

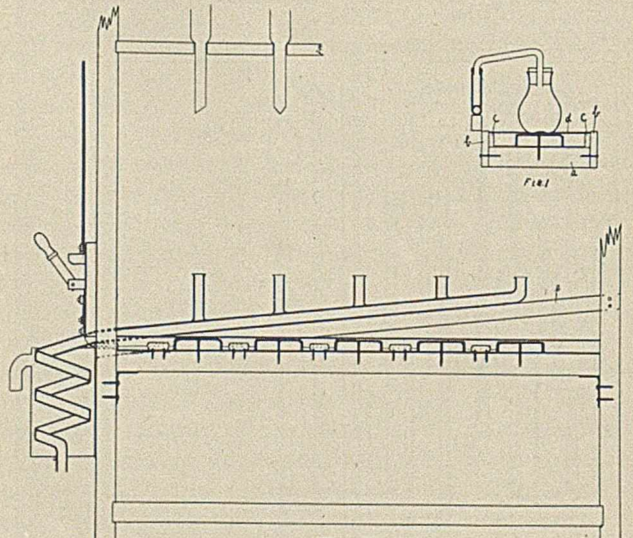

Fig 1

Fig 2

to distil off and collect the solvent after extraction has been completed and obviating the need of a separate apparatus for this purpose. The details of construction are represented in the three accompanying draw-figures, which represent transverse, longitudinal and horizontal projections of the lower portion of the apparatus.

The Bed of the Apparatus.—The bed (*a* of Fig. 1) which supports the five separate units consists of a board 5 x $^3/_4$ x 24 inches resting on metal cleats, fastened to the vertical supports as shown in Fig. 2. Two strips of wood (*b* of Fig. 1) 1$^3/_4$ x $^1/_4$ x 24 inches are nailed to the extreme edges of this support, and two wooden cleats (*c* of Fig. 1) $^3/_4$ x $^1/_4$ x 24 inches are fastened to the base as shown in Fig. 1. The space between the wooden cleats is covered with a strip of one-sixteenth inch asbestos board, and upon this are placed the five heating plates, which are held in position by screws passing into the base. The wooden cleats support a copper plate (*d* of Fig. 1) 5 x $^1/_{32}$ x 24 inches, which is provided with five circular openings of a diameter slightly greater than that of the heating plates. This plate is not fastened in place and can be readily removed for the purpose of inspecting or repairing the heating device.

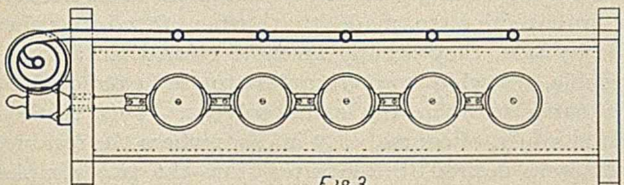

Fig 3

The Heating Device.—The heating plates were made from the caps used to close the ends of inch and a half water pipes by cutting with a hack-saw to a height of a half inch. These plates are heated by the current carried by a nichrome wire 0.01 inch in diameter which passes from a switch attached to one of the vertical supports through a circuit which includes three complete turns around each of the heating plates. The wire is insulated from the plates by means of strips of mica; it is held in its proper position by means of brass clamps fastened to the bed of the apparatus, each clamp holding two pieces broken from the stem of a Rose crucible, through which the wires are strung. The details of the wiring are best shown in Fig. 3. The total length of wire used was 150 inches and the total resistance offered was calculated to be 72 ohms. An actual measurement of the current consumed gave one and one-half amperes. All the plates were found to be uniformly heated and the heat generated was sufficient to cause ether to boil violently after the switch had been closed for ten minutes. A high boiling-point liquid in one of the flasks attained a temperature of 125°, but no difficulty was experienced in reducing this temperature by interposing a thin piece of asbestos between the heating plate and flask.

The Condensing Apparatus.—A strip of wood (*e* of Fig. 2) $^3/_4$ x $^1/_2$ x 26 inches, nailed to the back of the two vertical supports, sustains the condenser. The latter was made of block-tin tubing a half inch in external diameter and provided with five lateral upright branches, each soldered in place with pure tin. It terminates in a worm condenser, which is enclosed in a cylinder of sheet copper three inches in diameter placed at the end of the vertical support. Connection between the different flasks and the lateral opposite them is easily made by means of a glass tube fitted with cork stoppers as shown in Fig. 1. The entire device takes up but little room and in no way interferes with the use of the apparatus during extraction. Distillation and extraction can be carried on simultaneously on different heating plates provided the laterals of the condenser which are not in use are closed with cork stoppers.

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NOTES ON A NEW FORM OF EXTRACTION THIMBLE.[1]

By P. A. Boeck.

Received January 2, 1912.

The following notes have been collected from the experiences of a number of different investigators, using the new type of inorganic extraction thimbles known as "Alundum."

A few words as to the nature of these thimbles may be of interest: Alundum, the material from which these articles are made, is the product of the fusion of the mineral bauxite (a natural hydrate of aluminum carrying small percentages of iron oxide, silica and titanium oxide) in the electric furnace, in which process partial purification takes place so that the resulting product is essentially pure fused alumina. This material has been used quite extensively for abrasive purposes, replacing emery and corundum, over which it has the advantage of being absolutely uniform and of easily controlled composition. It can be made to yield an abrasive higher in crystalline alumina and consequently of higher abrasive efficiency than any other form of commercial, natural aluminous abrasive.

In the manufacture of laboratory articles of this material, the fused alumina is crushed, graded to uniform mesh, mixed with a small amount of a suitable ceramic bonding material and burned at a high temperature in an ordinary porcelain kiln, where the bond is caused to vitrify or mature, giving it the strength of an ordinary porcelain body, and at the same time retaining its porous nature, which allows the penetration and filtration of liquids and gases.

The porosity of the bodies can be controlled in several ways, which depend, to a certain extent, on the other physical properties, such as strength, thermal conductivity, texture, melting point, expansion due to temperature changes, shrinkage, etc., which are desired. The three methods most generally used in obtaining bodies of different porosities are: (1) by varying the size of the grain or particles of the alundum, thereby changing the size of the voids;

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[1] Presented at forty-fifth meeting of the American Chemical Society, at Washington, December, 1911.

(2) by changing the kind; and (3) the amount of bonding materials used. By combining these factors, suitable bodies may be obtained having any texture or porosity for the penetration of liquids of any density. The state of subdivision of the residue which is to be separated from the liquid or gas is of course the final criterion of the permissible size of the voids. In organic extraction work it is particularly desirable to have a porous medium, which gives the most rapid filtration possible with the complete retention of the residue.

Another feature of these thimbles is the fact that no blank extractions have to be made to be sure that the materials are fat-free, as in the case of paper or other organic materials, as, being of a refractory nature, they can be readily cleaned by being ignited at a temperature high enough to dispel any organic material. This also allows of their repeated and indefinite use, so long as no easily fusible inorganic material is ignited in them.

Messrs. Ross and Benner in their work at the Agricultural Experiment Station at the University of Arizona, on the filtration of soil solutions and the separation of "black alkali" in certain characteristic western soils, showed that filters of this material not only filtered more rapidly without changing the concentration of the solution and absorbed less than any other type of filter on the market, but required less washing, were very much more durable and could be cleaned and sterilized by igniting at the proper temperature. For further details, I would refer you to the original paper which is being read in another section of this meeting.

For the extraction and filtration of tanning materials, Mr. R. C. Oberfell describes in the *Journal of the American Leather Chemists' Association* for November, 1911. an ingenious device in which a porous Alundum dish substitutes the asbestos mat, or the mixtures of asbestos and kaolin, for removing the insoluble material in tanning materials. Absolutely clear filtrates were obtained in from 1/2 to 2 minutes without the use of any asbestos or kaolin mixtures in these dishes as against from 82 to 130 minutes using the official method of filtration with the mat, at a consequent saving of about 98 per cent. of the time of filtration, the results of the analyses in each case checking within the allowable error. Where the dish alone was used, no previous saturation or preparation of the filtering medium was necessary, as is the case in the official method.

For organic extraction work on rubber, vulcanized products, fats, waxes, soaps, bitumens. cereals, etc., the proper filtering body for any solvent can be easily made and is apparently limited only by the texture, which must be fine enough to retain the residue and prevent it from penetrating the pores of the thimble. Rapidity of flow and extraction can in this way be increased many times over that obtained with the ordinary extraction thimble.

The chemist of a large rubber reclaiming plant in the west has recently had made an ingenious type of thimble consisting of two thimbles semi-circular in cross-section so made that when fitted together side by side, they occupy no more room than a single thimble, allowing two samples to be extracted at the same time in the same solvent. This method would apply, of course, only in cases where the residues only were desired, the filtrates from the two samples being mixed. The scheme worked out very well at a great saving of time and solvent, and there is no reason why this idea could not be followed out further, and any number of sectional extraction thimbles made to fit one extraction tube.

The application of this type of inorganic extraction thimble has not been limited to liquids, as recent tests indicate that it can be used successfully for the filtration of gases and the separation of dust and fume from air, smoke, producer gas, etc., quantitatively.

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ADDRESSES

FERTILIZER CHEMISTRY—A REPORT OF PROGRESS.[1]

By PAUL RUDNICK.

Received January 12, 1912.

While it is too early to obtain figures on the consumption of fertilizers in this country for the year just passing, all indications justify the belief that there has been the usual material increase over the tonnage consumed in the previous year, which was estimated, in round numbers, at about 5,750,000 tons, an increase of about 14 per cent. over that of 1909. The average increase in the consumption of commercial fertilizers in the past decade has been something over 11 per cent. annually.

This material increase in the consumption of commercial fertilizers naturally brings up the question of materials entering into this commodity.

The production of organic ammoniates, such as blood, tankage, etc., cannot, under present conditions, keep pace with the greatly increased demand for them. The consumption of nitrate of soda is, of course, keeping pace proportionately with the increased consumption of commercial fertilizers in general. The consumption of cyanamide in this country shows a decided growth, and a plant for its manufacture is now being operated in this country at Niagara Falls. Other products of the utilization of atmospheric nitrogen, such as basic calcium nitrate, do not appear to have gained a foothold in this country as yet. While the annual production of sulfate of ammonia has been greatly increased with the increased installation of retort coke ovens, a great deal more of this valuable ammoniate could be assimilated easily. From the standpoint of conservation of our resources the time should be close at hand when the nitrogen

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[1] Chairman's address delivered before the Division of Fertilizer Chemists, American Chemical Society, December 27, 1911.

in practically all the coal consumed will be saved and converted into ammonium sulfate. It is exceedingly interesting to realize that practically all coals contain sufficient sulfur to combine with the nitrogen for production of ammonium sulfate and two different processes are now operated commercially on this plan.

It is a well recognized fact that organic ammoniates must be used in commercial fertilizers in addition to the inorganic ammoniates because of the demand for good mechanical condition, that is, a commercial fertilizer must work in the seed drill or other distributing apparatus without clogging. It is obvious, therefore, that with the increased consumption of commercial fertilizers, there must also be an increased production of organic ammoniates to meet with this requirement. Since the production of organic ammoniates has not been able to keep pace with the increased consumption of commercial fertilizers, very careful thought and study will be required to prevent exclusion of suitable materials by arbitrary methods of analytical control. Unless we can expand our supply of organic ammoniates, the cost of this very necessary class of fertilizer ingredients, which has already increased by leaps and bounds owing to the greatly increased demand, will soon become prohibitive. From a conservation standpoint, it also becomes imperative to utilize any organic nitrogenous material which is now going to waste, if it can be so treated or produced, that it can be shown to have a proper fertilizer value.

There is another point which may well be brought out in this connection, namely that experience has shown that varying availability in the ammoniates of a complete commercial fertilizer is highly desirable, so that there shall be more or less available nitrogen for the plant during the greater period of its growth and not only immediately after the application of the fertilizer.

A great deal of work has been done on the question of making the phosphoric acid in phosphate rock available by cheaper and more efficient means than by acidulation with sulfuric acid. None of the many proposed processes for this purpose, however, has as yet proved sufficiently satisfactory to be operated commercially. Under existing conditions, basic slag is practically confined to the Eastern States. It is to be hoped that a suitable method for producing available phosphoric acid from phosphate rock, other than by acidulation with sulfuric acid, will soon be discovered.

More experimental evidence that phosphate rock itself cannot be used profitably as a fertilizer is accumulating right along. The proposal to use a source of phosphoric acid of little or no availability is in striking contrast to the demand for high availability in the sources of nitrogen, even if the great difference in unit cost is considered.

In this connection the important role of sulfur recently brought out by the Wisconsin Agricultural Experiment Station is of the greatest interest. It is stated that some crops require even more sulfur than phosphoric acid and that the superior results obtained with acid phosphates over other phosphates may not be due entirely to a difference in availability but to the additional sulfur supplied by acid phosphate in the form of calcium sulfate.

Germany continues to be practically the only valuable source of supply of potash salts, and the German potash controversy is so familiar to all that it need only be mentioned in passing. One of the results of this controversy has been to stimulate the search for sources of soluble potash salts in this country to the greatest activity. In spite of repeated denials it appears certain that the source of potash recently announced in Maryland deposits is feldspar and that the proposed method of treatment consists in heating with salt and niter cake. The consensus of opinion, at the present time, is not favorable to the idea that it is possible to utilize feldspar as a profitable source of potash. Fusion or calcination with sodium or calcium compounds causes a material reduction in the percentage of potash, which is already low enough at best in the feldspar itself. The cost of lixiviation and concentration is admittedly prohibitive. The question of utilizing water-insoluble potash is being agitated even in Germany. One of the German Agricultural Experiment Stations reports successful results from the use of finely ground phonolith, apparently a product of the weathering of feldspar, somewhat similar to the zeolites in its nature. Other investigators, however, were unable to obtain such results and insist that this material is worthless as a source of available potash.

The report that the Department of Agriculture had located deposits of soluble potash salts seems to have been premature; it is now understood that sources, not deposits, were meant. It is also announced in this connection that the U. S. Geological Survey has begun actual field operations in the search for deposits of soluble potash salts. A well is being sunk at Fallon, Nevada, and it is to be hoped that the search will prove successful. A coöperative laboratory has been established at Reno, where prospector's samples will be examined. The possibility of finding commercial potash deposits in the arid regions of the west seems to be further indicated by the fact that potassium nitrate is usually present in considerable proportions in alkali soils and indeed the finding of small deposits has been repeatedly reported. The most recent report indicates that such deposits were located in Idaho. So far such deposits have been very small and of very low potash content.

The functions of manganese and boron in the soils are of interest from a fertilizer standpoint. The results so far reported seem to indicate that their function is a catalytic one.

In this connection it is important to note that the A. O. A. C. at its meeting this year adopted as a provisional method a modification of the official method for determining water-soluble potash, consisting in leaching out the water-soluble potash from the sample with hot water much in the same manner that water-soluble phosphoric acid is removed in the determination of insoluble phosphoric acid. Considerable work has been done on this subject by the Committee on Potash of this Division and the results of the work of this committee indicate that the modified method will give much more nearly the actual proportion of potash put into the fertilizer by the manufacturer. In the official method an average of 0.3 per cent. of water-soluble potash becomes insoluble in the course of extraction.

The theory of the action of fertilizers continues to engage the efforts of many research workers both in this country and abroad as a part of their work on the biochemistry of soils and plants. It has become very evident that the plant food theory is inadequate. Applications of commercial fertilizers which produce large and profitable increases in crops are not nearly sufficient in all cases to replace the elements removed by the plants from the soil. Much attention has been attracted to the discoveries regarding the presence in soils of protozoa which live on and destroy beneficial soil bacteria, of fungi which are harmful either directly to the plants or perhaps to the soil bacteria and of the toxic action of certain constituents of the soil which are either excreted by the plant roots themselves or may be produced by decomposition in the soil. It is easy to believe that fertilizers may exert a beneficial action on the soils to which they are applied by suppressing the activity or harmfulness of such organisms or substances, but it does not follow that this constitutes the entire explanation of the action of fertilizers. The idea that fertilizers may act in part by rendering soluble or otherwise releasing unavailable elements of plant food from the soil is plausible, but lacks confirmation and cannot in any event explain completely the mechanism of the action of fertilizers.

It is more than likely that the theory advanced by Dr. Cameron at our meeting a year ago, namely that no simple explanation can be hoped for, but that the entire matter is enextricably bound up with a large number of other modifying factors such as climatic and meteorological conditions, tilth, drainage, seed selection, etc., is the best we have at present.

It may be well to point out in this connection another possible partial factor in the action of fertilizers. Loeb (*Science*, **34**, 653 (1911)) recently announced that the presence of both potassium and calcium chlorides in sea water is necessary because they exert a protective action on the organisms with which he experimented. These organisms die very quickly in pure distilled water or in a pure sodium chloride solution, as well as in a pure cane sugar solution, and somewhat less quickly when potassium chloride is present in addition to sodium chloride. When both potassium and calcium chlorides are present, however, in addition to sodium chloride, the animals can live for several days. The best proportion of these three salts is that existing in sea water and it is of interest to note that the relative proportion of these salts in human blood is the same as in sea water, although the concentration in blood is much less.

Taking into consideration the fact that practical experience has shown complete fertilizers to be almost uniformly of much more proportional value in producing increased crop yields than incomplete fertilizers, is it not possible that at least a part of the action of complete fertilizers may consist in a similar protective action of their soluble constituents on the cells of the plant? That some action of this sort exists would seem to be further indicated by the results of the extensive researches published on the calcium-magnesium ratio in soils.

With the enormous amount of research work now being carried on in this field, it seems quite likely that we shall soon come to a fairly comprehensive and clear understanding of the more important phases of the mechanism of the action of fertilizers in producing crop increases, so that the most efficient manner of application may be determined with a reasonable degree of accuracy by scientific methods. This is a problem in which producer and consumer alike are interested and its solution will constitute an important chapter in the conservation of our resources.

Efficiency has come to be an important watchword in our every-day life, and much has been accomplished in this direction in agriculture by the use of improved farm machinery. President Taft, in his address on "Conservation of the Soil," before the National Conservation Congress, at Kansas City, last September, quoting from the Yearbook of the Department of Agriculture for 1898, pointed out that between the years 1855 and 1894, the time of human labor required to produce 1 bushel of corn declined on an average from 4 hours and 34 minutes to 41 minutes, and the cost of the human labor required to produce this bushel declined from 35$^3/_4$ cents to 10$^1/_2$ cents. Between 1830 and 1896 the time of human labor required for the production of a bushel of wheat was reduced from 3 hours to 10 minutes, while the price of the labor required for this purpose declined from 17$^3/_4$ cents to 3$^1/_3$ cents. Between 1860 and 1894, the time of human labor required for the production of a ton of hay was reduced from 35$^1/_2$ hours to 11 hours and 34 minutes, and the cost of labor per ton was reduced from $3.06 to $1.29. In 1899 the calculation made with respect to the reduction in the cost of labor for the production of seven crops of that year over the old-time number of production in the fifties and sixties shows it to have been $681,000,000 for one year. But while it is possible to say that in the future there may be improvements in machinery which will reduce the number of necessary hands on the farm, it is quite certain that in this regard the prospect of economy in labor for the future is not to be compared with that which has been effected in the last 30 years.

To these words of President Taft I wish to add that much profitable progress has also been made in the selection of seeds and in the material and profitable increases of crop yields from the use of commercial fertilizers. While the use of commercial fertilizers commonly shows a material profit, there is doubtless much fertilizer used wastefully because unscientifically. Greater efficiency in this respect can be developed only on the basis of a scientifically accurate theory of the action of fertilizers.

CURRENT INDUSTRIAL NEWS

By W. A. Hamor.

PROGRESS OF THE CHEMISTRY OF PAPERMAKING.

Arthur D. Little presented a full report on this subject at the Thirty-fifth Annual Meeting of the American Paper and Pulp Association, February 15, 1912 (see *Paper* 6, No. 10, p. 25), from which the following material is taken.

As in a number of other industries—*e. g.*, in glass manufacture—paper-making in the United States is still too frequently regarded as a hereditary art, while in Germany it has become a science. The extent to which the industry has established itself upon a scientific basis is evidenced in the special number of the *Papierfabrikant*, published in June, 1911, and "the publication as a whole cannot fail to impress any thoughtful American paper-maker with the seriousness of the competition which he will ultimately be called upon to meet." Further evidence of the status of paper-making in Germany is had from the 1911 *Proceedings of the Verein der Zellstoff und Papier Chemiker*, wherein abstracts of 305 scientific studies covering almost the whole field of pulp- and paper-making are given, and "at least one other volume will be required to complete the record for the year."

The report of William Raitt, cellulose expert to the India Provinces Exhibition of 1910, published in 1911, contains results of studies on about forty specimens of wood to determine their suitability for pulp-making. These investigations included trial cooks by the standard chemical processes, and Riatt found the sulphate process most generally effective. Riatt concluded that the following species offer the most promising fields for further investigation: *Picea morinda* (spruce); *Abies pindrow* (silver fir); *Bombax malabaricum*; *Trewia nudiflora*; *Salix tetrasperma* (willow); and *Butea frondosa*. His study of the Indian grasses shows that several of these are available in large quantity and furnish excellent sources of paper stock; and he also found that the sulphate process, at any rate with certain species, is adapted for the reduction of bamboo, yielding pulp of such good color that it is immediately available for half-bleached papers. The subject of bamboo as a substitute for wood is to be exhaustively studied at the Indian Forest Research Institute, Dehra Doon. This is of especial interest to Americans in that Richmond has called attention to Philippine bamboo as one of the most promising substitutes for wood for paper-making. Richmond prefers the soda process for its treatment and reports the yield to be 45 per cent.

The straw paper industry, which is highly developed in France, has been described by Abadie. Many different kinds of paper are produced from straw, and in the Limousin paper is made from this material without cooking. Manufacturers in the southwest of France cook the straw in rotary digesters for about four hours with milk of lime.

American paper-makers have been urged to give a more general consideration of esparto, which, according to the experience of English paper-makers, stands in a class by itself as a raw material for the manufacture of high-grade book papers. Great quantities of esparto remain untouched in Algeria for lack of a market. The fiber from the inner bark of the baobab or monkeybread tree is also "deserving of more general utilization." Among other materials, cottonwood is said to yield about 43 per cent. of absolutely dry fiber by the sulphite process.

The most important development of 1911 in connection with paper-making is considered to be the prospect opened out by the new Simmons sugar process of obtaining bagasse or waste sugar cane fiber in great quantities and in a form particularly available as a raw material for paper-making. The large supply of waste fiber obtained under the new process is substantially free from pith, is reduced very easily by the soda process, and yields a pulp suitable for the manufacture of book and printing papers. Cornstalk or maize fiber is said to still have its advocates.

The year marks no notable technical advance in the manufacture of sulphite fiber, but nevertheless considerable attention has been given to the problem of the utilization of waste sulphite liquors. The most important development in this direction is a process introduced in Sweden wherein an impure grade of ethyl alcohol is produced by fermentation of the waste liquor after neutralization with lime. However, this process holds out no hope of avoiding the nuisance created by the waste liquors, since distillery-slop is far more objectionable than the original waste liquor, owing to the presence in it of large quantities of dead yeast. In Germany, attempts are being made to utilize concentrated lyes, after eliminating the sulphurous acid, for cattle feed, but such utilization has not so far been found profitable. The employment of a concentrated liquor for tanning in connection with tannin extracts continues to a certain extent. A method of utilization entitled to careful study is that of Vögel, who recommended that the waste liquor be evaporated, mixed with coal, and then burned. "Saduyn," prepared from the waste lyes of sulphite mills, treated at about 100° C. with sodium chloride, is said to be used in the form of a solution for saturating porous material for the absorption of the vapors of acrolein and other gases in the exhaust of motor cars. Two kg. of the powder is stated to be sufficient for a motor vehicle run of 600 km.

The chemistry of the sulphate process was discussed by Klason and Segerfelt (*Papierfabrikant*, September, 1911). These authors point out that the yields of fiber by the sulphate method are about 50 per cent., while those by the soda process are 37 per cent. With regard to the formation of mercaptan in the sulphate process, it has been proposed that this compound be destroyed by nitrous gases.

At Skutskar, Sweden, the Rinman soda process is in use; soda is recovered by precipitating the organic matter from the waste liquor by means of carbon dioxide in the presence of sodium chloride, and the precipitated material is distilled for the production of acetone and wood alcohol.

It has been proposed that Epsom salt be substituted for alum in rosin sizing. Pauli and also Klemm conclude that, although magnesium sulphate is not to be regarded as a complete substitute for alum, it may replace a considerable proportion of the alum used when used concurrently therewith. Little points out in this connection that in most mills much more alum than is necessary is commonly used.

In coloring, indanthrene blue has been introduced as a substitute for ultramarine. When this dye is employed, it is said to be possible to obtain a back water free from color.

It has been pointed out by Lehman that the waste water loss from paper mills frequently amounts to 10 per cent. of the materials used, and that of this loss fully 90 per cent. is recoverable, even by simple sedimentation methods.

Little urges the establishment of a school of paper-making in this country. It is stated that the matter has been taken up by the Boston Paper Trade Association.

RECENT INVESTIGATIONS ON ALLOYS.

Advance proofs of papers to be presented before the Institute of Metals, issued January, 1912, contain much of interest to the industrial chemist. Abstracts of several of these follow.

Rosenhain, in a discussion on the "Nomenclature of Alloys," directs attention to the confusion which exists at present in the naming of alloys, especially in the use of the terms "brass" and "bronze," which are sometimes employed in contradiction. A system is suggested in which the class name "brass" includes all alloys whose principal constituents are copper and zinc, and "bronze" those containing copper and tin; and when other metals are present, each particular alloy is distinguished by a prefixed addition to the class name, for example, the so-called "Aich metal" would be termed "iron brass" and "manganese bronze" would be known as "manganese brass."

Bengough, in a paper on the "Properties of Alloys at High Temperatures," gives determinations, through ranges of temperature up to their melting-points, of the influence of temperature on the breaking tensile stress and elongation of copper and aluminum, alloys consisting of a single, simple, solid solution (copper-nickel, 70 : 30 brass), and alloys consisting of two solid solutions or other phases (Muntz metal; low-copper brass). In every instance the author finds that the tensile strength diminishes as the temperature rises, although there is generally a change of direction in the curve representing this, most marked in the pure metals (copper, 650° C.; aluminum, 395° C.). Above these temperatures the metals resemble very viscous fluids, possessing little strength, being very ductile, and greatly influenced in their tensile strength by the duration of the application of stress. Stress also causes them to emit a cry like "tin-cry." There are no thermal critical points at these temperatures, and Bengough suggests that in a pure metal the crystals are normally held together by Beilby's "amorphous material," stronger than themselves, in a more or less continuous sheet or cellwork, and that above the "temperature of recuperation" this is no longer capable of existing, and the crystals accordingly come in contact with one another. Fracture now occurs, no longer through the crystals, but along the crystal faces. When a metal is worked at a temperature above the point of recuperation, "amorphous material," if formed, cannot exist permanently, and no effect is produced on the mechanical properties of the metal: this is "hot work." "Cold work," conducted wholly or partially below this temperature, produces "amorphous material" and strengthens the metal. Bengough shows the difference between rolled and cast material in strength by diagrams, and it is seen to vanish at the temperature of recuperation. In the case of pure metals, the elongation may increase, diminish, or remain almost constant, up to the point of recuperation, but there it greatly increases, and remains high until near the melting point.

Turner presents a study of the "Behavior of Certain Alloys when Heated *in vacuo*." He has found that zinc and other metals are entirely removed from brass and other copper-zinc alloys when the latter are heated in a vacuum. With brass, the separation of the zinc is quantitative provided the temperature does not exceed 1200° C. and the heating is not too prolonged. A sample of "poisoned" brass was subjected to this treatment, and it was found that all the zinc, lead and arsenic, and a little of the tin, were removed at 1200° C. Zinc was readily volatilized from 60/40 and 70/30 brass at temperatures of 520° and 550° C., respectively; and when "hard zinc," the residue from galvanizing baths, containing about 5 per cent. of iron, was heated to 500° C., in a vacuum, the zinc was completely volatilized, the iron remaining entirely in the residue. This paper is of great importance on account of the suggested application of the principle to the refining of crude copper, brass scrap, hard zinc, etc.

SILOXIDE

"Siloxide" is a name which has been given to products prepared by fusing pure anhydrous silica with oxides of elements of the silicon-carbon group, as titanium dioxide or zirconium oxide. The new glass is said to be formed by the solution of these refractory oxides of an acid character in silicic acid, and it is stated to be more easily worked than pure quartz glass—in fact, it can be worked by the ordinary methods employed in glass manufacture (see French Patent 432,786, July 31, 1911, of Wolf-Burckhardt and Borchers). Z-siloxide, or zirconium glass, and T-siloxide, or titanium glass, are now being manufactured at Frankfurt a/M, Germany.

While Z-siloxide and T-siloxide are said to lack the silky luster of quartz glass ("vitreosil"), yet it is stated [Thomas, *Chem.-Ztg.*, 36, 25 (1912)] that they possess distinct advantages over the latter with respect to strength, resistance to devitrification, and resistance to the action of alkalies.

The best Z-siloxide with respect to strength is said to contain 1 per cent. of zirconia, while that containing 0.5 per cent. has the most satisfactory thermal properties. It is said that zirconium glass has a softening point not much different from that of quartz glass, but that it resists deformation better at high temperatures because of its greater viscosity. The manufacturers state that zirconium glass crucibles are far superior to those made of quartz material in their ability to resist the action of "oxide-bearing metals" during smelting operations; that zirconium glass can be used five or six times; and that it displays only in a very small degree the disagreeable property, inseparable from quartz material, of devitrifying at temperatures exceeding 1300° C. It is supplied in the form of tubes, slabs, concentrating vessels, crucibles, flasks, boxes, muffles, arched-tubes, balls, calottes, etc.

The titanium glasses (0.1 to 2 per cent. of titanium) are said to have a somewhat lower resistance to compression than quartz glass, but to resist transverse fracture better than the latter. The T-siloxide now being marketed is said to be superior to even Z-siloxide with respect to thermal properties—to be more satisfactory when temperatures up to 1500° C. are to be used. Its properties are said to be otherwise the same as those of Z-siloxide. While it is stated by the manufacturers that zirconium glass may be had either transparent or opaque, no information on this point as to titanium glass was secured.

EXTRACTION WITH NAPHTHALENE.

Naphthalene has been known for some time as a solvent for gums and resins (see, for example, English Patent, 14,554, June 30, 1903, to Terrisse), and as a substitute for benzine and benzene, and similar solvents, for spreading purposes in the manufacture of rubber goods (see French Patent, 393,186, August 10, 1908, of the Rütgerswerke-Akt.). Quite recently, a Magdeburg-Sudenburg, Germany, firm has placed on the market a plant for the extraction of bones, plants, fish residues, asphalt, etc., with naphthalene.

As is well-known, naphthalene is volatilized by means of steam; it is this property, in fact, which makes it advantageous as an extractive medium. Temperatures from the melting point, 80° C., to almost the boiling point, nearly 218° C., are said to be applicable; and if this is correct, it is possible to work within wide limits. Further advantages are said to be that the solvent can be recovered from the solutions at relatively low temperatures in comparison with other solvents with similar boiling points; that it is not necessary to employ closed vessels with reflux condensers; and that the use of pressure, generally necessary for dissolving copals, may be dispensed with in the apparatus.

The naphthalene extraction process is said to be particularly applicable for the extraction of bitumen, as "larger quantities of a product of higher melting point are extracted by naphthalene from asphalt-sand or Montan-wax than if one of the ordinarily known extraction substances is used." In one test, 90 per cent. benzene was used, and 19 per cent. of bitumen with a softening point of 70° was obtained; while with the naphthalene process, 23 per cent. of bitumen with a softening point of 81° was obtained from the same material in a shorter period. It is said that for the extraction of asphalt, the low price of the raw material is a consideration. In addition, it is stated that no losses are incurred and that it is not necessary to resort to such high temperatures that a partial decomposition of the product occurs, in order to effect the separation of the solvent from the asphalt.

The naphthalene process is reported to be of particular value if the bituminous rock, bones, plants, etc., are mixed with about one-half their weight of naphthalene and then extracted by heating. For this purpose, impure naphthalene may be used; it is afterwards recovered as pure naphthalene by treatment with steam.

FIRE EXTINCTION.

The use of frothy mixtures for fire extinction has recently been investigated at Wilhelmsburg, near Hamburg, Germany, in the presence of officials representing the Prussian Fire Brigade (see *Preuss. Feuerwehr-Beirat, Drucksache*, No. 4, 1911; *Engineering*, January 12, 1912, 52. A solution of sodium hydroxide, containing froth-forming ingredients, and a solution containing alum and other chemicals, are mixed together by means of carbon dioxide, which results in the production of a foam consisting of bubbles filled with carbon dioxide; the foam is then directed on to the surface of burning petroleum, tar, etc. It is reported that 2 l. of the mixed liquids, when directed on to light petroleum spirit, gave 13 l. of foam, the volume of which diminished by 5 per cent. in 5 minutes, 14 per cent. in 10 minutes, 47 per cent. in 30 minutes, and 76 per cent. in 1 hour. In one series of tests, the plant employed comprised two reservoirs each of 5 cm. capacity, from which the solutions were delivered to the mixer by two duplex feed pumps at the rate of about 160 l. per minute. The foam was discharged from the mixer through a pipe of 80 mm. diameter, which branched into two pipes of 52 mm. diameter. Fifteen tons of crude petroleum benzine were ignited in a brickwork tank of 10 m. diameter, and after the fire had burned for 5 minutes in a strong wind, the foam was applied under a pressure of 2 atmospheres. The fire was soon stifled except for isolated jets of flame near the edge of the tank, and completely extinguished in 6 minutes; after 10 minutes, on removing the layer of foam, the benzine could be immediately relighted. About 1800 l. of the mixed liquids were consumed. The results seemed to demonstrate that it was advantageous to apply the foam under a low pressure in order that it might spread quietly over the burning surface. Another test was made on burning tar with satisfactory results.

NOTES AND CORRESPONDENCE

THE CENTENARY OF THE INTRODUCTION OF GAS.

The 100th anniversary of the introduction of the use of gas as an illuminant will be celebrated in Philadelphia on Thursday and Friday, April 18th and 19th, 1912. The exercises will be held in the Hall of the Franklin Institute, 15 South 7th Street, and will take the form of a symposium under the auspices of The American Philosophical Society, The Franklin Institute, The American Chemical Society and The American Gas Institute.

PROGRAM.

Thursday: **"By-products in Gas Manufacture,"** by Chas. E. Munroe, at 8 p.m.

Friday: **"The Commercial and Financial Aspects of the Gas Industry,"** by George B. Cortelyou, at 10 a.m.

"The Technic of Gas Manufacture," by Alfred E. Forstall, at 11 a.m.

"Gas as an Illuminant," by Van Rensselaer Lansingh, at 2 p.m.

"The Use of Gas for Heat and Power; the Testing of Gas," by Edward B. Rosa, at 3 p.m.

These lectures will constitute an interesting and valuable review of the development of the use of gas as an illuminant, and as a source of heat and power. Persons interested in the manufacture and use of gas from all parts of the country, members of the societies named, and the general public, including ladies, are cordially invited to attend the sessions.

An effort will be made to bring together as many as possible of the pioneers in the gas industry, those who have been engaged in the industry thirty years or more. All such are requested to send their names to the acting secretary.

A temporary *Loan Exhibition* will be held in the Hall of the Franklin Institute, of articles, models, appliances, books or pictures, that have an historical interest. Any one who knows of such articles should communicate at once with the Acting Secretary, William J. Serrill, 1401 Arch Street, Philadelphia.

AMERICAN ELECTROCHEMICAL SOCIETY, TWENTY-FIRST GENERAL MEETING, BOSTON, APRIL 18th to 20th.

PROGRAM.

The Effect of Addition Substances in Lead Plating Baths. By F. C. Mathers and O. R. Overman.

Uniformity and Simplicity in Electrochemical Calculations. By Carl Hering.

Effects of the Variations of Thermal Resistivities with the Temperature. By Carl Hering.

Experiments on Heat Insulation. By F. A. J. FitzGerald.

An Electrolytic Method for the Reduction of Blue Powder. By Warren F. Bleecker.

Tensile Strength of Electrolytic Copper on a Rotating Cathode. By C. W. Bennett.

The Regeneration of Sulphated Storage Cells. By C. W. Bennett and D. S. Cole.

A Rotating Cathode. By C. W. Bennett.

Electrical Endosmose. By W. D. Bancroft.

On the Nature of Zinc Cementizing (Sherardizing). By Arden R. Johnson and Willis R. Woolrich.

Smee's Theory of Electrolytic Deposits. By W. D. Bancroft.

Power Supply to Electric Furnaces for Refining Iron and Steel. By W. Sykes.

Furnace Electrodes Practically Considered. By R. Turnbull.

On the Volatility of Zinc Oxide. By O. L. Kowalke.

High Tension Equipment for Electrometallurgical Plants. By J. R. Wilson.

The Influence of Diffusion on the Electromotive Force Produced in Solutions by Centrifugal Action. By W. Lash Miller.

Vacuum Furnace Metallurgy. By C. G. Fink.

Temperatures of the Carborundum Furnace. By L. E. Saunders.

Gas Circulation in Electrical Reduction Furnaces. By J. W. Richards.

Potential Differences at the Junction of Unmiscible Phases. By R. Beutner.

Performance of Dry Cells. By C. Hambuechen.

Report of the Committee on Dry Cell Tests.

AMERICAN COMMISSION ON ORGANIC NOMENCLATURE.

An American Commission on Organic Nomenclature has been appointed, consisting of the following:

M. T. Bogert, Columbia University, Chairman; Ira Remsen, Johns Hopkins University; W. A. Noyes, Univeristy of Illinois; T. B. Johnson, Yale University; M. Gomberg, University of Michigan; J. F. Norris, Simmons College; J. B. Tingle, McMaster

University; C. H. Hudson, Bureau of Chemistry, Washington, D. C.

This commission will coöperate with similar National bodies in other countries in the revision of the Nomenclature of Organic Compounds.

Suggestions as to the general plan to be pursued in undertaking this work, or concerning special groups of compounds, will be welcomed, and should be sent to the Chairman at Columbia University.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

Abstract of Announcement No. 3.

This announcement includes the following of special interest and importance:

Ladies' Committee, Committees on Internal Transportation, Entertainment, Finance, Papers and Publications, Trans-Atlantic Transportation, Factory Inspection.

Rules on Papers, their Presentation, Discussion and Publication.—Papers and their abstracts, both in duplicate, must be in the hands of the American Committee not later than June 30, 1912, in order to assure their inclusion, if accepted, in their respective Sectional Volumes for distribution at or before the opening of the Congress.

The Congress obligates itself to have its final Reports and Proceedings, including subject and author index, completed and ready for distribution on or before December 31, 1912.

Rejected manuscripts are to be returned to their authors and all correspondence concerning them is to be regarded as strictly secret and confidential.

How to Obtain Membership in this Congress.—Membership in this Congress is open to individuals, corporations, societies, associations, institutions and the like.

Persons contemplating membership in the Congress can obtain membership tickets from the Treasurer of the Congress, Wm. J. Matheson, 182 Front Street, New York City, by forwarding to him an application for membership and the membership fee, which is $5.00. Membership tickets can also be obtained from Prof. M. O. Forster, 84 Cornwall Gardens, London, S. W., England; M. F. Dupont, 6 Place Malesherbes, Paris, France; Dr. B. Rassow, Stephanstrasse 8, Leipzig, Germany; Prof. Rosario Spalling, Via Panisperna, 89 bis, Rome, Italy.

Membership of Congress Committees does not constitute membership in the Congress.

All memberships received after July 15, 1912, by the American Committee, are accepted on the condition that delivery of printed reports cannot be guaranteed to such members.

Entertainment of Ladies.—The arrangements herefor are in the hands of the Ladies' Committee, and everything will be provided by them to insure the comfort, convenience and entertainment of all ladies attending the Congress. Applications for *Ladies' Tickets*, together with the fee therefor, $3.00, should be sent to William J. Matheson, 182 Front Street, New York City.

Program of Meetings.—The general lectures are to be given by (1) George M. Beiley, of Glasgow, Scotland, "Some Physical Aspects of Molecular Aggregation in Solids;" (2) Gabriel Bertrand, of Paris, France, "The Role of Very Small Amounts of Chemical Substances in Biochemistry;" (3) Carl Duisberg, of Elberfeld, Germany, "The Latest Achievements and Problems of the Chemical Industry;" (4) Giacomo Ciamician, of Bologna, Italy, "Photochemistry of the Future;" (5) Ira Remsen, of Baltimore, Md., U. S. A. (subject to be announced later).

General lectures and general meetings will be held in the Great Hall of the College of the City of New York; Sectional meetings at Columbia University. The Columbia University Gymnasium will be headquarters for Registration, Distribution of Papers, Distribution and Sale of Tickets, Information Bureau, Telephone, Messenger, Telegraph and Cable Services, and Post Office Express and Baggage Facilities.

Columbia University furnishes not only places of meeting and other conveniences as noted above, but also has placed at the disposal of attending members living outside of New York the use of certain of its Residence Halls from August 31, 1912 to 10 A.M., Friday, September 13, 1912. Applications for quarters in these Halls should be addressed to the Eighth International Congress of Applied Chemistry, Residence Hall Committee, 25 Broad Street, New York City.

A list of selected hotels and suggestions for accommodation of parties.

Information concerning excursions and visits to works.

Excursions.—Arrangements in this direction are tentative and very incomplete and the excursions finally selected will depend upon the number of members indicating their desire to join the respective excursions. The itineraries of eight different routes ranging in cost from $11.70 to $435.00 and in duration from 7 days to 44 days are submitted. All of these prices are based upon parties of not less than 100 and do not include hotel charges nor transportation to and from hotels. A map inserted at the end of the pamphlet shows the routes contemplated.

Special Notice.—For the accommodation of those who wish to visit Yellowstone Park, a special tour has been provided for, leaving New York not earlier than August 10th, and not later than August 15th, and requiring about thirteen days with no factory inspection. Members intending to take this tour must notify the Transportation Committee not later than May 15, 1912. Members intending to take part in any of the other trips, must notify the Transportation Committee not later than June 15, 1912. All communications in relation to tours should be directed to "*Transportation Committee,* Eighth International Congress of Applied Chemistry, P. O. Box 1625, Philadelphia, Pa."

Visits to Works.—The list comprises 321 different establishments, located in 144 different cities, and representing 139 different industries or branches thereof. It will, of course, be impossible for the Congress to visit all of these on excursions or set trips. Individual members or small parties of members will be granted permission to visit, by any of the works on the list and not visited by the Congress on excursions or set trips, on presentation of the Treasurer's receipt for membership dues.

Rules governing admission to factories are very strict especially as to visits by *competitors.* Some works will admit competitors but negotiations for such inspection *must be made* by and through Prof. M. C. Whitaker, Chairman, Factory Visits Committee, Columbia Univeristy, New York City.

Special Steamship Accommodations and Rates.—The European participants in the Congress are urged to reserve their accommodations for the westward trip at the earliest possible moment, since the steamships are apt to be very crowded at that season of the year.

CORRECTION.

A CONVENIENT FILTERING APPARATUS.

In the issue of This Journal for March, 1912, page 222, under the article whose title is given above, the name of the author was given as C. S. Williams, Jr., instead of C. S. Williamson, Jr.

THE BUSINESS ASPECT OF THE KELP PROPOSITION.

By Frederic P. Dewey.

Received February 17, 1912.

It is thoroughly well established that the giant kelps of the Pacific provide an enormous store of KCl. Various papers have appeared upon the broad, general aspect of the question, but for the most part they have dealt in glittering generalities and many of them have started in the middle of the proposition. Many writers neglect or slur over the gathering and preliminary drying of the kelp, and base their real consideration of the subject upon the air-dried material. This is very attractive and easy to do, but the cost of the air-dried kelp is a most serious business consideration.

There are various technical and business problems connected with the matter. Without in the least doubting the eventual solution of these problems, it may be said with entire safety that their solution with financial profit will require the expenditure of much time and money, under the best technical and business direction, and that it must be several years before KCl from kelp can become a commercial commodity, if it ever does.

The consideration of the subject divides itself naturally under the following heads:

Harvesting the kelp.
Air-drying.
Oven-drying.
Distillation.
Crystallizing KCl.
Marketing.

To start with the growing kelp. How can it be harvested? It will be an entirely new industry and manifestly various machines of different types will have to be constructed and subjected to actual practical tests before an efficient and economical machine is secured. Dr. Cameron[1] has suggested 1,000,000 tons of KCl as a conservative annual yield. This would mean the harvesting of approximately 30,000,000 tons of kelp. This harvesting cannot extend over the whole year. Just how long it may last cannot yet be definitely known, but in any event the vast machinery required to harvest 30,000,000 tons in a short season must stand idle a good part of the year at a heavy interest charge against the product.

Having brought the kelp to shore it must be dried. To produce a ton of KCl, approximately 27 tons of water must be evaporated. Clearly the most inexpensive natural means for drying must be adopted, but even this would require the construction of drying sheds covering an enormous area and the building of especially designed machinery to distribute the wet kelp on the drying shelves and to gather up the dried stuff. As with the harvesting machinery, these sheds and machinery must remain unemployed a good part of the year.

There is, however, a limit to the extent that natural drying in open sheds can be carried. When about 25 tons of our 27 tons of water have been evaporated, provision must be made to protect the efflorescing KCl which will soon be produced on further drying. This will require the application of artificial heat. It may possibly be assumed that this can be obtained from the kelp itself in a subsequent operation. By proper oven-drying it is possible to recover 40–50 per cent. of the KCl as effloresced salt by simply shaking it off from the dried kelp.

The recovery of the balance of the KCl from the dried and shaken kelp requires the breaking up of the organic matter of the kelp body and this must be done with as full as possible utilization of its value. Simple burning with the utilization of its heat value only will not be sufficient, even if we now had a furnace adapted to avoid enclosing unburned material in the inorganic salts by sintering and to avoid undue loss of KCl by volatilization.

At present, there does not seem to be any method available for this part of the work except destructive distillation with the recovery of the condensable by-products and the utilization of the gas, first to heat the retorts, and secondly, for the oven-drying of the kelp as far as may be. Probably there are no technical difficulties in this operation, but it must be remembered that only about half of the weight, including the effloresced KCl, of the oven-dried kelp is organic matter. In other words, broadly speaking, in the production of one ton of KCl only one ton of organic matter is available for the production of by-products of distillation. On the other hand, the total production of such by-products in the recovery of 1,000,000 tons of KCl would be so large that much of them would have to be transported long distances to find a market and therefore the profit of the operation would largely depend upon freight conditions.

Undoubtedly a limited amount of the residue from the retorts could find direct application as a fertilizer within a certain radius, but the real market for KCl is on the Atlantic coast, and under the present freight conditions of 80 cents per 100 lbs. the KCl must be dissolved and recrystallized. Upon the opening of the Panama Canal and the expected halving of the freight rates, the distillation residue might possibly better be shipped direct.

The mother liquors from the recrystallizing of the KCl will contain iodine and when sufficiently enriched they may be treated for the recovery of this element.

It would be a liberal estimate to assume that the by-products recovered including the iodine, would have a value sufficient to pay for all of the operations upon the air-dried kelp. If we do this and also assume that after sufficient trial and development of the necessary machinery the kelp can be harvested for 25 cents per ton and air-dried for 15 cents per ton more, a ton of KCl laid down on the Atlantic coast would cost $28 as follows:

Harvesting 30 tons at 25 cents..............	$7.50
Air-drying 30 tons at 15 cents..............	4.50
Freight 1 ton at 80 cents per 100 lbs.........	16.00
	$28.00

On the completion of the Panama Canal it is expected that the freight will come down to $8 per ton, but the present prices of KCl must be very profitable to the German Potash Syndicate and if actually faced with the possible loss of its American trade the prices would undoubtedly be reduced. This reduction might even wipe out the advantage of the low water-freight.

In conclusion it would appear that the feldspars have not yet been displaced by the kelps as a possible source of potash.

Washington, D. C.,
February 16, 1912.

IMPORTATIONS OF ACETIC ANHYDRIDE.

The importation of acetic anhydride, which for some years has been steadily on the increase, is showing since last March a very rapid decline, according to the figures published by the quarterly report of the Department of Commerce and Labor on Imported Merchandise Entered for Consumption in the United States. The amounts in pounds imported during the quarters ending at dates given and their valuations are as follows:

Sept. 30, 1910, 202,227 lbs., $38,531; Dec. 31, 1910, 266,204 lbs., $50,838; March 31, 1911, 504,536 lbs., $93,501; June 30, 1911, 197,518 lbs., $35,806; Sept. 30, 1911, 117,093 lbs., $20,842.

This sharp decline in the consumption of acetic anhydride is probably due to the abandonment of the manufacture of cellulose acetate films for photographic purposes.

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[1] This Journal, 4, 77.

CONSULAR AND TRADE NOTES

ENGLISH MUNICIPAL GAS WORKS.

Consul Edward B. Walker, Burslem, advises that the report for the year ended March 31, 1911, of the gas department of Stafford, population 25,000, contains some interesting information and figures. The gas works have been in the possession of the municipal corporation for 33 years, during which time the bonded indebtedness has been reduced from $550,673 to $182,189, a reserve fund has been provided, and municipal taxes have been reduced $286,019. The price of lighting gas is $0.65 per 1,000 feet, with discounts up to 10 per cent. according to consumption, and $0.48 per 1,000 feet for power, with discounts up to 25 per cent., reducing the price all around to about $0.37.

The gross receipts during the year in question were $162,899 and the expenditures $93,930, leaving a gross profit of $68,969. Loans repaid, interest, etc., amounted to $31,447, and the net balance was distributed as follows: District fund in reduction of taxes, $17,033; free library, $243; suspense account, $6,083; reserve fund, $9,755; carried forward, $4,408. The town had a profit-sharing scheme under which the workmen received a bonus of over 10 per cent. of their wages. The amount of gas sent out was 211,852,000 feet, of which 4,358,630 feet was unaccounted for, or leakage. The coal used was Staffordshire "washed beans," costing about $2.68 per ton.

The gas business is managed and treated as a separate undertaking. All salaries of officials and expenses of management and operation are included in the balance sheet, and the corporation pays taxes as would an ordinary company.

UTILIZATION OF NATURAL GAS IN HUNGARY.

Consul-General Paul Nash, Budapest, advises that it is not known exactly what are the intentions of the Hungarian Minister of Finance as to the utilization of the natural gas in Transylvania, several million cubic yards of which have already escaped, but it is likely that before the end of the year the gas will be in use in one or more of the towns and industrial plants in the immediate vicinity of the wells. The gas-producing region comprises some 5,800 square miles, and the Government has so far put in over 20 wells, varying in depth from 1,000 to 3,300 feet. It is thought that the supply of gas will last for at least 50 years.

Eventually the gas will be brought to Budapest, although probably not for a few years. In any case, as soon as it appears that the public is to have natural gas placed at its disposal, there will be an immediate demand for meters, purifiers, pipes, valves, stoves, burners—in short, everything used in the exploitation of natural gas. There is no reason why American manufacturers, if they employ the proper methods, should not have the bulk of this business, as the American preëminence in this line of manufacture is generally recognized in this country. Everything points to the development of a large business. Manufacturers should send representatives to study the field and personally choose agents.

SWEDISH COAL SITUATION.

Consul Stuart J. Fuller, Gothenburg, reports that the threatened scarcity of imported coal, due to the labor troubles in England and the augmented demand owing to the lack of water for power, is bringing about increased activity in the Swedish mines in Skane, in the south of the Kingdom. The Skane coal is not suited for coke and is of inferior quality. It is conceivable that the labor troubles in England might affect the situation to an extent such that Sweden would have to look elsewhere for its supply, thus giving a possible opportunity for the introduction of American coal.

Coal constitutes nearly 10 per cent. of the total imports into Sweden. About one-fifth of this fuel is entered at Gothenburg, which port and Stockholm are the principal import places, Malmo and Gefle coming next. The total import for the last three years for which figures are available has been, in tons: In 1907, 4,146,785; in 1908, 4,427,507; in 1909, 4,084,055. It was practically all from Great Britain. The kinds in 1909 were, in tons: Anthracite, 146,162; gas and coking, 263,749; smithy and nut, 300,258; steam coal, 3,352,943; miscellaneous, 20,943.

The production of coal in Sweden is less than 7 per cent. of the consumption of the country, the output in 1910 being 302,800 tons.

CORK TRADE OF THE UNITED STATES.

The cork-growing industry is being introduced experimentally into the United States by the Department of Agriculture. At Chico, Cal., the Bureau of Plant Industry has growing quite a number of cork-oak trees of various species that were secured by David Fairchild, the Department's agricultural explorer. The Bureau of Forestry is also conducting experiments near Pensacola, Fla., where the Cork-oak acorns have been planted, some of which are growing in the second year successfully.

Lacking a native supply, the United States purchases abroad nearly $6,000,000 worth of raw and manufactured cork, official statistics for the calendar year 1911 showing imports of unmanufactured cork wood or bark, valued at $3,819,651, and of cork manufactures worth $2,070,672, a slight decrease from the respective totals of $3,908,533 and $2,191,563 in 1910.

MALAYSIAN TIN EXPORTS.

The Federated Malay States Government Gazette gives the following table to show the weight of tin (tin exported in the form of ore having been taken at 70 per cent. of the gross weight of the ore) exported from the Federated Malay States during 1910 and 1911 (picul = 133$^{1}/_{3}$ pounds):

	1910.			1911.		
States.	Tin. Piculs.	Tin contained in tin ore. Piculs.	Total. Piculs.	Tin. Piculs.	Tin contained in tin ore. Piculs.	Total. Piculs.
Perak........	109,867	311,468	421,335	97,835	339,504	437,339
Selangor.......	43,397	196,795	240,192	54,215	176,960	231,175
Negri Sembilan	121	34,576	34,697	90	29,140	29,230
Pahang.......	12,930	27,744	40,674	15,281	28,673	43,954
Total.......	166,315	570,583	736,898	167,421	574,277	741,698

SHARK'S LIVER OIL INDUSTRY PROPOSED.

Vice-Consul General D. Milton Figart, Singapore, Straits Settlements, states that it has been proposed to start in Malaysia a small export trade in shark's liver oil. This oil is refined in Europe and sold as cod-liver oil. In October the ocean sharks come into the lagoon, between the barrier reef and the atolls, to pair. At this time they can be speared in large number by people skilled in catching them. There are several species of these sharks and they ordinarily run from 7 to 15 feet in length. The girth of an ordinary shark is the same as its length, and an 11-foot shark would be 11 feet around the body. The liver of a shark of this size gives about 5 gallons of oil. The oil brings $73 a ton. The sharks are found in pairs and the harpooners try to kill the male first, in which case they are able to also spear the female, as it does not desert its mate.

BOOK REVIEWS

Transactions of the American Institute of Chemical Engineers. Vol. III (1910). 8vo., 411 pages. D. Van Nostrand Co., New York, 1911. $6.00.

Contents: Evolution of Portland Cement Processes, Chas. F. McKenna. Study of Materials in Chemical Engineering Chas. F. McKenna. Reports of the Committee on Chemical Engineering Education, F. W. Frerichs. Remarks on Chemical Engineering Education, F. W. Frerichs. Development of the Chemist as an Engineer, F. W. Atkinson. The Training of Chemical Engineers which Meets the Requirements of Manufacturers, M. C. Whitaker. Teaching Industrial Chemistry, A. H. Sabin. Commercial Manipulation of Refractory Elements for Incandescent Lamp Purposes, Ralph E. Myers. The Manufacture and Industrial Applications of Ozone, Oscar Linder. The Changes in Industrial Chemistry Caused by Electricity, E. R. Taylor. Notes on the Corrosion of Iron and Steel and its Prevention, G. W. Thompson. Protal; a New Product for Use in the Arts, F. G. Wiechmann. Chemical Industries of Canada, J. C. De Cew. Underground Waters for Manufacturing Purposes, Wm. M. Booth. Loss in Coal Due to Storage, A. Bement. Nitric and Mixed Acids, Schuyler Frazier. Plant Design, Wm. M. Grosvenor. The Fitzgibbon Boiler, J. Alexander. Manufacture of Hydrated Lime, R. K. Meade. Bleaching Oils with Fuller's Earth, David Wesson. SYMPOSIUM ON SEWAGE DISPOSAL. Principles of Sewage Disposal, G. C. Whipple. Sewage Disposal in Europe, Rudolph Hering. Sewage Disposal in New York City and Vicinity, G. A. Soper. Sanitary Conditions in their Relations to Water Supplies in the Vicinity of New York, N. S. Hill, Jr. Unsolved Problems of Sewage Disposal, C. E.-A. Winslow.

It speaks well for the activity of our youngest chemical society, that in the third year of its existence, it can produce such an imposing array of papers as the table of contents shows.

The volume, which shows the usual excellent work of the publishers, as well as evidence of careful proof-reading, contains much to interest not only the chemical engineer, but also the chemist who is not an engineer. The teacher of chemistry and the civil and the sanitary engineer will find much to interest them.

Aside from the papers on Chemical Engineering Education and allied subjects, all of which are of intense interest, the following are especially worthy of note:

Evolution of Portland Cement Processes, by Chas. F. McKenna.

The Manufacture and Industrial Applications of Ozone, by Oscar Linder.

Plant Layout, by W. M. Grosvenor and the Symposium on Sewage Disposal. D. D. BEROLZHEIMER.

The Technology of Bread-Making, including the Chemistry and Analytical and Practical Testing of Wheat, Flour and Other Materials Employed in Bread-making and Confectionery. By WILLIAM JAGO, F.I.C., F.C.S., AND WILLIAM C. JAGO. American Edition, Bakers' Helper Company, Chicago. 908 pages; 123 figs.

The present volume, as stated by the senior author in his preface, is a development of his previous works on the same subject which appeared in 1886 and 1895. The large amount of research in the field of bread-making since 1895 has caused the authors to make a complete revision of the earlier editions.

The general scope of the new volume and the relative importance which has been placed upon separate subjects are indicated in the following brief synopsis of the 33 chapters:

An elementary treatise upon inorganic and organic chemistry with special reference to ash, fat, carbohydrates, and proteids, 120 pages.

Enzymes, fermentation and the technology of yeast, 130 pages.

The chemistry of wheat, flour, and milling products, 150 pages.

The chemistry of bread and bread-making, 125 pages.

Nutritive value of bread and laws governing its sale, 50 pages.

Bake-house design and baking machinery, 100 pages.

Methods for analysis of flour, bread, confectioners' raw materials, etc., 220 pages.

Index, 15 pages.

In addition to the results of their own researches and experience, the authors have collected a wealth of material hitherto scattered in scientific journals, experiment station bulletins, court records, etc., of different countries and have added to this a great deal of information gathered from private sources. In reviewing the recent work in their field, the authors have prepared brief abstracts of all original articles which they have supplemented by a critical review. This method of treatment is particularly commendable and though the reader may not, in all cases, agree fully with the opinion of the authors upon some disputed points, he will find the arguments *pro* and *con* presented with equal fairness and fulness of detail.

In addition to its value to those specially interested in the bread-making industry this new volume will be of great service to the food chemist and public analyst. The chemist in preparing testimony for a court will find valuable assistance in the discussion of such topics as bread improvers, faulty bread, alum baking-powders, bleached flour, and scores of other subjects which might be mentioned.

The description of chemical methods is upon the whole very complete although the reader may, in certain cases, wish that in naming the author of a particular method the reference to the original publication had always been given for his guidance. The quartz wedge saccharimeter is used at present more extensively than the polarimeter in the analysis of food products and a short description of this instrument should have been included in the polariscopic methods of analysis.

The book is well printed and the cuts and photographs clear and distinct. C. A. BROWNE.

Die Chemie der trocknenden Oele. By WILHELM FAHRION. 8vo., pp. viii + 298. Berlin, Julius Springer, 1911. Price, 10 M.; cloth, 11 M.

The author calls attention to the fact that the greater importance of drying oils over all other forms of fatty bodies is indicated by the publication in 1867 of J. G. Mulder's work on "Die Chemie der Austrocknenden Oele" before the publication of any works devoted to the general chemistry of fats and oils.

The present work is a comprehensive review of the chemistry of drying oils brought well up to date. The principal part of the text is devoted to linseed oil, the other drying oils being very briefly treated.

In the present work, the literature of the subject appears to have been gone over very thoroughly, at least so far as it has been published in German or English, and reference is made throughout to the original papers. The subject is treated principally from the standpoint of the analyst, comparatively little material having been introduced from descriptions of manufacturing processes unconnected with analytical processes. To the analyst this work will be a convenient book of reference.

PARKER C. McILHINEY.

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian, Chemists' Club, New York.

Analysis, Rapid Methods of—. By N. Samter. L. 8vo., 237 pp. $2.50. Halle, 1911. (German.)

Bread, The Chemistry of— Making. By J. Graut. 8vo. $1.25. London, 1912.

Cellulose, The Chemistry of—, with Special Reference to the Textile and Similar Industries. By C. G. Schwalbe. L. 8vo., 680 pp. $6.25. Berlin, 1912. (German.)

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Chemistry, Triumphs and Wonders of Modern—. By Geoffrey Martin. 8vo., 378 pp. $2.00. D. Van Nostrand Co., New York.

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Fuse, Investigations of— and Miners' Squibs. By Clarence Hall and Spencer P. Howell. 8vo., 19 pp. U. S. Bureau of Mines, Technical Paper 7.

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Roasting, The Important Factors in Blast—. By H. B. Pulsifer. *Metallurgical and Chemical Engineering*, Vol. 10, 1912, No. 3, pp. 153–159.

Rubber, Ceresin Wax in— Mixings. By W. J. Britland and H. E. Potts. *India Rubber Journal*, Vol. 43, 1912, No. 7, pp. 5–9.

Sewage, Note on the Phenol-Sulfonic Acid Method of Determining Nitrates in— Effluents. By Harry Silvester. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 3, pp. 95–96.

Sugars, A New Method for the Determination of Reducing—. By E. C. Kendall. *Journal of the American Chemical Society*, Vol. 34, 1912, No. 3, pp. 317–341.

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Zinc, An Electrolytic Method for the Reduction of Blue Powder. Advance Copy. By Warren F. Bleeker. *Transactions American Electrochemical Society*, Vol. 21, 1912.

RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

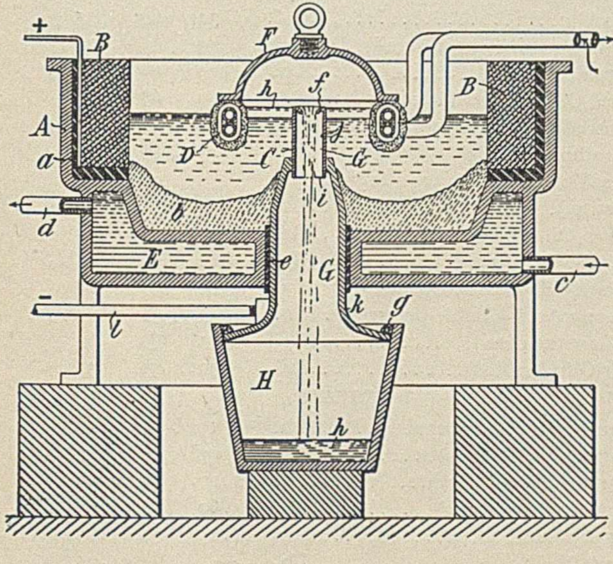
ELECTROLYTIC APPARATUS.

U. S. Patent No. 1,007,897, to G. O. Seward and F. von Kugelgen, Virginia.

This invention relates to an electrolytic cell or vessel for the production of metals lighter than their electrolytes.

In the production by electrolysis of those metals and alloys which have a less specific gravity than the molten electrolytes from which they are separated, a source of difficulty is the collection of the metals in such a way that they cannot come in contact with the gases set free at the anode, with which they would otherwise combine.

The present apparatus is designed to render possible and easy isolation of the separated metal or alloy by providing a combination of a cathode projecting up from the bottom of the electrolytic vessel through the electrolyte, and a chilled salt-incrusted collecting partition located above the cathode in such a way that the metal is confined as soon as separated and can be allowed to collect within the chamber or space bounded by such partition, from which it may be removed as convenient.



In the production of sodium, which remains fluid at the temperature of the electrolyte, difficulty is presented in discharging the metal from the cathode chamber into a suitable receiving vessel, by reason of the congealing of the metal upon the walls of the conduit which becomes clogged thereby.

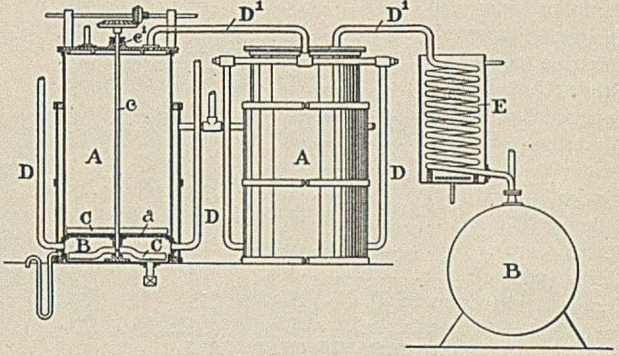
The invention provides for the ready discharge of such fluid metal by providing a vertical conduit into which the metal flows from the cathode chamber over a spout or lip which causes it to fall freely through the conduit without touching its walls, or touching only those portions of its walls which are adequately heated. This conduit is preferably formed integral with the cathode by making the latter hollow.

MANUFACTURE OF FERRIC OXIDE.

U. S. Patent No. 1,008,321, to John Gill, England.

This invention is based on the fact that calcium carbonate can be changed into a soluble calcium bicarbonate and in the presence of a solution of ferrous chloride precipitates the iron contained in the liquor as ferrous carbonate which is capable of being oxidized into ferric hydrate.

The invention consists essentially in treating waste or other liquors containing ferrous chloride with carbonate of lime and carbon dioxide and air to precipitate into ferric hydrate and subsequently calcining the ferric hydrate to drive off the water and obtain a pure or high-class oxide of iron.

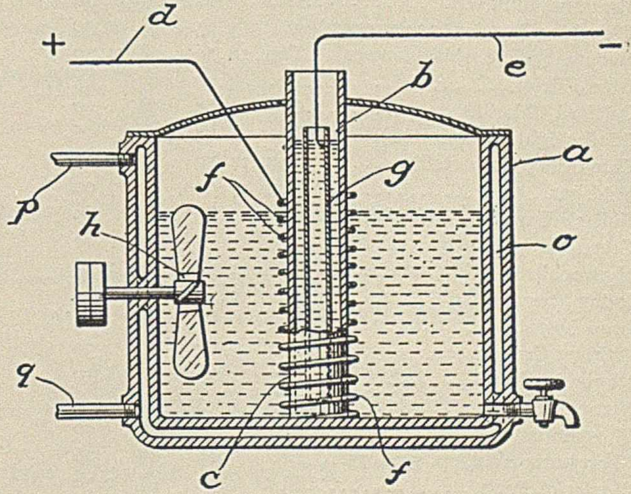


The accompanying illustration shows apparatus in which the process can be advantageously carried out.

PROCESS FOR CONVERSION OF LOWER OXIDS OF NITROGEN TO HIGHER OXIDS OF NITROGEN.

U. S. Patent No. 1,008,383, to Fin Sparee, Wilmington, Delaware. Assignor to the E. I. du Pont de Nemours Powder Co.

This is a method of treating oxides of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxides of nitrogen solution and acidulated water, between electrodes in the respective solutions, the current density on the electrode in the oxides of nitrogen solution being above one hundred amperes to the sq. cm. and the current density on the electrode in the acidulated water below ten amperes to the sq. cm.



The accompanying illustration shows apparatus in which the process can be advantageously carried out.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF MARCH.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	14½	@	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.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	1.87½	@	2.02½
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23½	@	28
Carbon Tetrachloride (drums)	Lb.	9¼	@	12
Carbon Bisulphide	Lb.	nominal		
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	18	@	19
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	—	@	44
Dextrine (imported potato)	Lb.	5½	@	5¾
Dextrine (corn)	C.	2.95	@	3.31
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	14¾	@	15
Oxalic Acid	Lb.	7½	@	7⅞
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.20	@	2.50
Starch (potato)	Lb.	5	@	5¼
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid, crystals	Lb.	30½	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.25	@	2.30
Acetate of Lead (brown, broken)	Lb	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8¼
Ammonium Chloride, gray	Lb.	6	@	6¼
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3½	@	3¾
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.45	@	1.60
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.25	@	1.30
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	4.90	@	5¼
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4½	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8⅛	@	8⅝
Lithium Carbonate	Lb.	67	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9¼	@	10
Potassium Cyanide (bulk) 98–99 per cent.	Lb.	19½	@	21
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4¾	@	5
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver	Flask	46.00	@	48.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	37	@	39
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5	@	5¼
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	2.20	@	2.22½
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	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.	12¾	@	13
Tin Oxide	Lb.	47	@	51
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

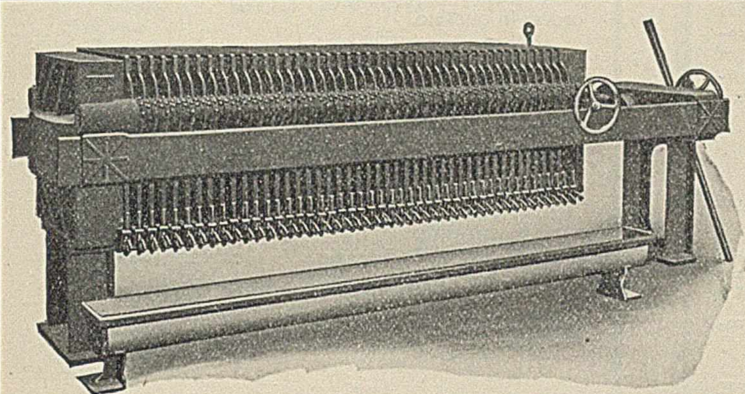
Beeswax (pure white)	Lb.	40	@	45
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	8	@	14
Corn Oil	C.	5.20	@	5.50
Cottonseed Oil (crude), f. o. b. mill	Gal.	34	@	35
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	9¼	@	9½
Lard Oil (prime winter)	Gal.	80	@	85
Linseed Oil (double-boiled)	Gal.	72	@	75
Paraffine Oil (high viscosity)	Gal.	23½	@	24
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3⅛
Rosin Oil (first run)	Gal.	38	@	40
Spindle Oil, No. 1	Gal.	14	@	14½
Sperm Oil (bleached winter) 38°	Gal.	76	@	78
Stearic Acid (double-pressed)	Lb.	8¾	@	9½
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	19¼	@	19½
Antimony (Hallet's)	Lb.	7⅜	@	7½
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	14.60	@	14.65
Copper (lake)	Lb.	14.65	@	14.75
Lead, N. Y	Lb.	—	@	4.05
Nickel	Lb.	40	@	45
Platinum (refined)	Oz.	45.50	@	46.00
Silver	Oz.	58¾	@	59⅜
Tin	Lb.	42⅜	@	43
Zinc	Lb.	6.85	@	—

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	—	@	3.30
Fish Scrap, domestic, dried	Unit	3.25	@	10
Blood, dried	Unit	2.85	@	—
Tankage, high grade	Unit	2.70	@	10
Bone, 4½ & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.05	@	—
Phosphate, acid, 16 per cent.	Ton	7.50	@	7.75
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13	@	0.13¼
Castor meal	Unit	2.95	@	3.10 & 10
Mowrah meal	Ton	8.50	@	9.00



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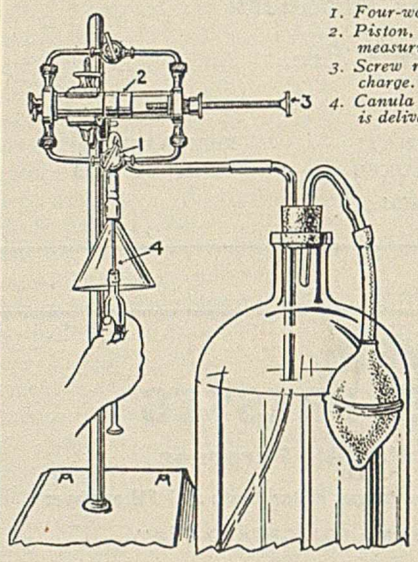

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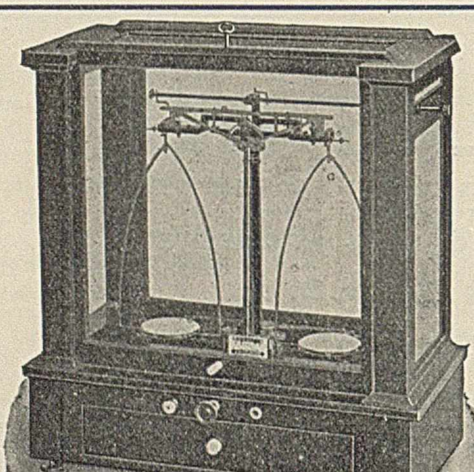

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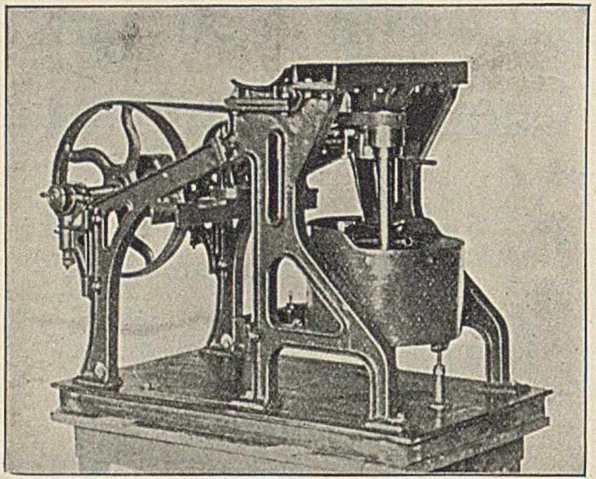

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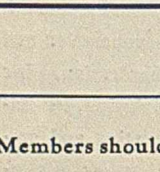

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GRADUATE CHEMIST, aged 26, thoroughly skilled and experienced in general analytical work, desires change. Place in or near Philadelphia, Pa., preferred. Address "Analyst," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 56-5-12

CHEMIST, with best technical training in a leading eastern university and two years' experience in petroleum refinery of one of the large companies, desires to change present position. Understands works operations. Excellent references can be furnished. Address "S. F. C.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 43-5-12

CHEMIST, experienced in manufacture of full line of varnishes, japans, enamels, and several self-selling specialties, would make connection with good concern. Has own laboratory and will match samples, furnish formulas, make analysis and test raw material. Moderate remuneration acceptable. Excellent references furnished. Address "Oils," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 42-5-12

CHEMIST, College graduate '05, experienced in cement laboratories and all work connected therewith, also in iron and steel analysis, desires to connect with good company. Excellent references. Address "W. D.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 48-5-12

POSITION wanted by graduate, B.A., of a large Eastern university. Experienced in the assaying, refining, and recovery of silver, gold, platinum and indium; also in the analysis of steels and fertilizers. Excellent references. Address "H. H.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 61-5-12

WANTED, position by young man graduating in June from chemistry department of a large university. Location immaterial. Address "A. E.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 62-5-12

A theoretically educated chemist with practical experience wishes to change his present position. Replies should be directed to F. Hofer, P. O. Box 665, Prince Albert, Sask., Canada. 63-5-12

FERMENTOLOGIST and food chemist desires a change of position. Seven years chief chemist of a large distillery, and for three years superintendent and distiller. Highest references. Address "J. X. S.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 47-5-12

RESEARCH CHEMIST, B.S., M.S., age 23, with three years' experience in research work in pure organic chemistry, desires a similar position in the industrial field. Position in the East preferred. Knowledge of French and German. Salary expected, $1200. Open to engagement June 1st. Address "F. P. G.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 46-5-12

INSTRUCTORSHIP or position of similar grade in organic chemistry wanted by Ph.D. ('11, leading Eastern University), beginning with academic year 1912-'13. At present studying abroad. For further information regarding previous teaching experience, references, etc., apply to "Alicyclic," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 45-5-12

CHEMIST, B.S., at present employed in metallurgical laboratory, desires a change of employment. One year's experience in iron, steel, brass, and ferro-alloy analysis. Broad, theoretical training in all branches of chemistry. Will accept position at moderate salary where ability and conscientious work will merit advancement. Excellent references. Address "W. L.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 50-5-12

FIRST-CLASS CHEMICAL ENGINEER, college graduate. Open for engagement about June first. At present employed. Eight years head chemist in cement factory. One year as head chemist in beet sugar house. One year as head chemist in sugar cane house. Familiar with machinery in both cement and sugar houses. German and Spanish spoken. Address "X.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 51-5-12

ANALYTICAL CHEMIST, Tufts '12, thorough knowledge of General Analytical Chemistry and Sanitary Water Analysis, desires position with some Manufacturing concern or Water Inspection Laboratory, where conscientious work and ability will meet appreciation. Salary, moderate to start. Address "R. H. B.," 29 Capen St., Tufts College, Mass. 49-5-12

CHEMIST AND METALLURGIST with practical knowledge of metallography. Ph.D. University of Wisconsin. Experienced in Textile, Inorganic, Alloys and Analytical work. Two years' experience on factory research problems. Reads French and German. Strong personality and executive ability. At present employed in inorganic research. Desires to connect with company operating along chemical lines in Southern states, Mexico, Central or South America. Can furnish best of references. Address "B. J.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 44-5-12

CHEMIST, with wide experience in Sanitary Water Analysis, Brewing, Fermentation, and Technical Chemistry, at present instructor in quantitative and of water analysis in an eastern college, desires to hear of position in either teaching or technical work. Address "W. E. R.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 55-5-12

CHEMIST and bacteriologist open for engagement—teaching or practical work. Laboratory and practical experience in vinegar, cider, jams, preserves, catsups, canning, etc. Have also taught at college. Address "Pure Foods," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 54-5-12

CHEMIST, University Graduate, Ph.B., formerly with large manufacturing concern, experienced in general investigation and testing of commercial products, organic and inorganic—paints, oils, lubricants, glass, clayware, assaying and technical analysis—seeks position in New York or vicinity. Moderate salary and excellent references. Address "F. S. H.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 53-5-12

WANTED, by student in leading Eastern university, a position in a chemical laboratory, beginning June, 1912. Has had a thorough training in analytical chemistry. Has experience in analyzing ores of all common metals, limestone, rock, coal and gas. References furnished. Address "D. J. B.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 52-5-12

CHEMICAL ENGINEER, who will graduate in June with degree of B.S. from a leading technical school, desires position offering opportunity for advancement. Three months' practical experience in oil and water analysis. Best of references. Address "J. A. H.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 58-5-12

UNIVERSITY INSTRUCTOR, B.S., M.S., Ph.D., desires summer work, preferably near Chicago, June 15th to Sept. 15th. Has had theoretical, practical and teaching experience in A. C. and D. C. electrical precision measurements, high temperature installation and measurements, thermal analysis of alloys, steels, etc. and photomicrography. Address "E. B.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 59-5-12

Ph.C. Mass. College of Pharmacy, '09, desires a change. At present and for the past year and a half with a large dairy company as chemist and bacteriologist. Would prefer position as assistant in bacteriological, hygiene or board of health laboratory, preferably the first. Willing to start on moderate salary, provided there is an opportunity to learn and advance. Address "T O. L.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 60-5-12

CHEMIST, with 19 years' experience in university teaching, technical work, also general analytical work, seeks a good position. Am at present employed but have excellent reasons for desiring a change. Address "Chemist A," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 31-4-12

RESEARCH CHEMIST, age 25, graduate from Technical School of Germany, D.S. (Doktor-Ingenieur), specializing in physical chemistry, electrochemistry, physics, desires position in electrochemical works or research laboratories in U. S. Ambitious, energetic, Frenchman. Speaks English, French, German, Hungarian, Servian. Good references. Address Dr. M. G., poste-restante (Hauptpost-lagernd), Aix-la-Chapelle, Germany. 28-4-12

CHEMIST, pharmaceutical, graduate of German University, desires to change position. Long, practical experience in food, water, pharmaceutical and general analysis. Familiar with clinical and bacteriological work. Expert in the analysis of toilet preparations, working out of new and original ideas. Can assist pharmaceutical concern in the manufacture of new lines, ampules, artificial baths, etc. At present and for the past eight years with one of the most prominent Eastern laboratories. A1 references. Address "C. B.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 29-4-12

GRADUATE CHEMIST, age 32, having a long experience in drug and chemical work, desires position offering opportunity for advancement. Place in or near Baltimore, Md. At present employed. Address "Chemist," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 25-4-12

CHEMIST, with five years' experience in miscellaneous analytical work in a commercial laboratory. Have had special training in water analysis and bacteriology at College. Desires a position. Address "L. E. B.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 26-4-12

EXPERIENCED YOUNG CHEMIST, with four years' experience in manufacturing baking powder and extracts, wishes industrial position where there is opportunity to advance. Can furnish best of references. Address "L. A. T.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 30-4-12

WANTED, by undergraduate student in Eastern technical school, a position in a chemical laboratory for the months of June, July and August, 1912. Can furnish best of references. Address "S. W., care Journal of Industrial and Engineering Chemistry, Easton, Pa. 34-4-12

CHEMICAL ENGINEER, B.S., Ph.D., of wide experience, at present in charge of manufacturing end of large chemical works, would like to make a change. Address "Argon," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 35-4-12

UNIVERSITY position desired by graduate of Wisconsin, B. S. Engr., M.S., Ph.D., in a reputable science and engineering college desiring to introduce course in applied electrochemistry and chemical engineering. Have had six years of university teaching experience in all phases of chemistry, pure and applied chemical research work, laboratory construction, etc. Address "Professor," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 36-4-12

CHEMIST, PhD., Yale, at present employed in connection with a metallurgical enterprise, desires a change of employment. Combines a broad theoretical training in all branches of chemistry with practical experience in analysis and metallurgy Thoroughly capable of handling research work in any line or of running a laboratory. Address "S. H.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 37-4-12

ASSISTANT CHEMIST in industrial laboratory desires to change within Philadelphia, for advancement. Graduate; over six years' experience in steel works laboratories and industrial laboratory; and experienced in iron and steel; familiar with ferro-alloys, alloys, coal and lubricants. A position either as head or assistant in an industrial laboratory preferred. Address "M. S. G.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 38-4-12

GRADUATE of Massachusetts Institute of Technology and Johns Hopkins University, at present assistant professor of organic and physiological chemistry and toxicology, desires to hear of position for teaching. Medical school preferred; experienced as teacher and in Clinical examinations, and with wide experience in sanitary chemistry and biology Address "H. S. F.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 39-4-12

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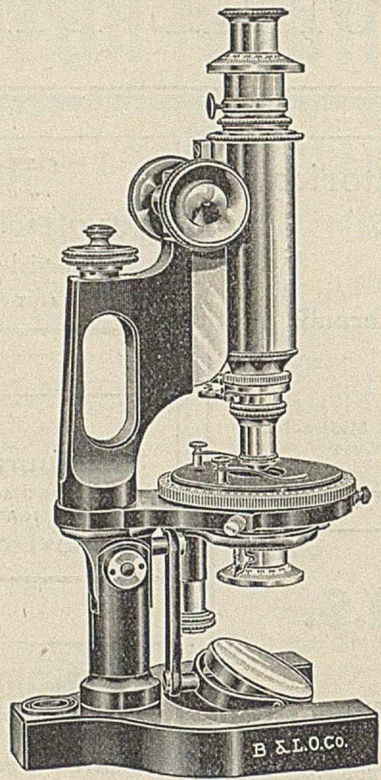
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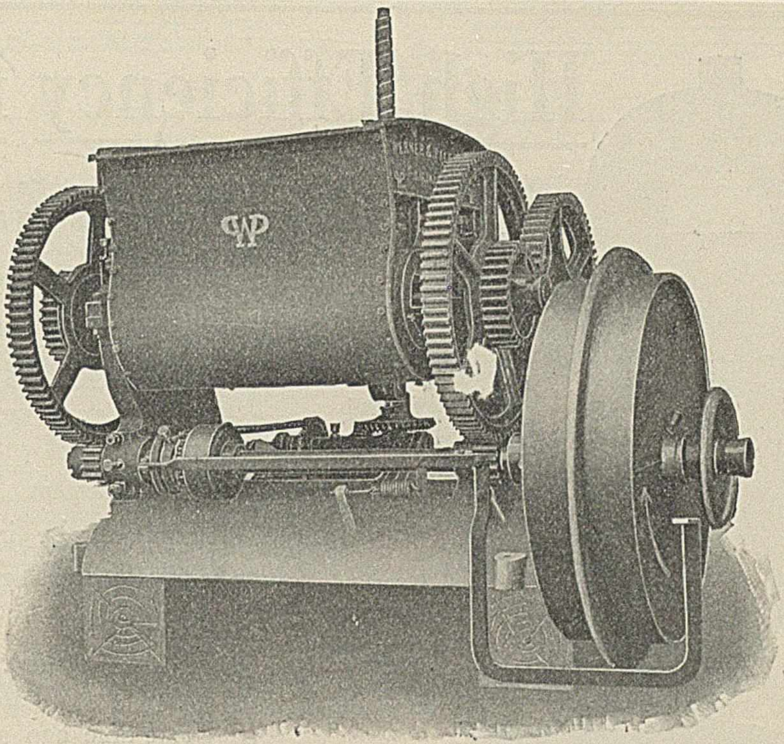

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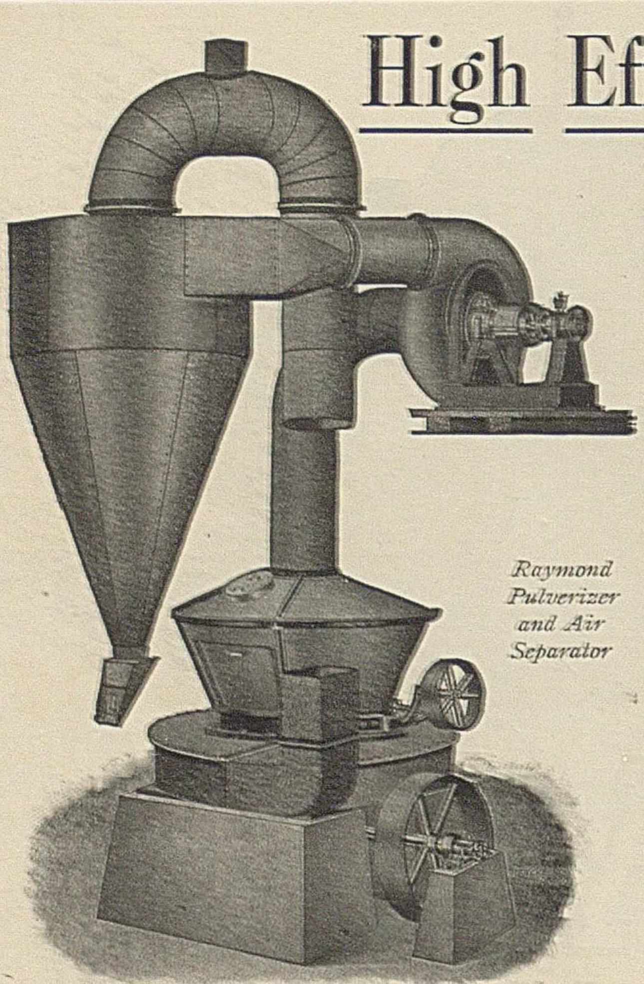

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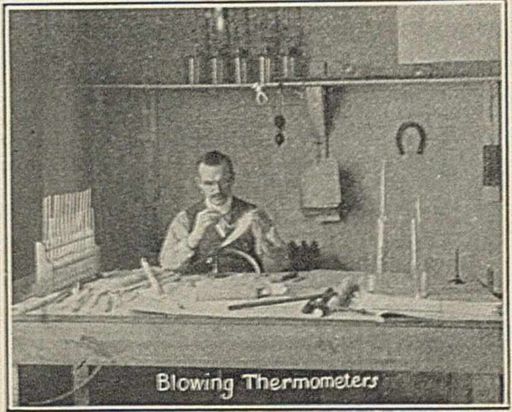
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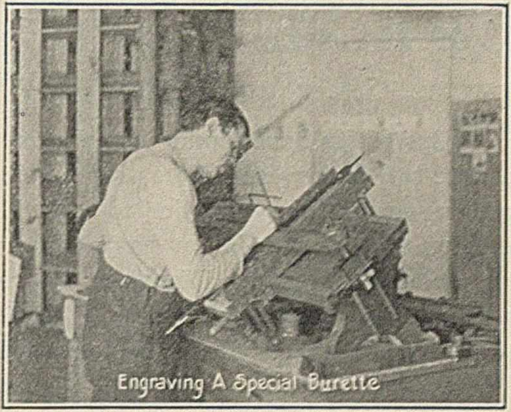
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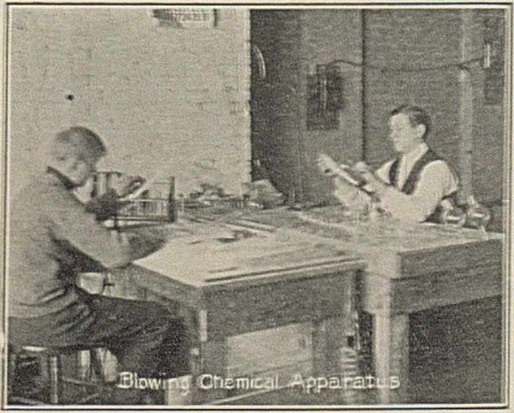
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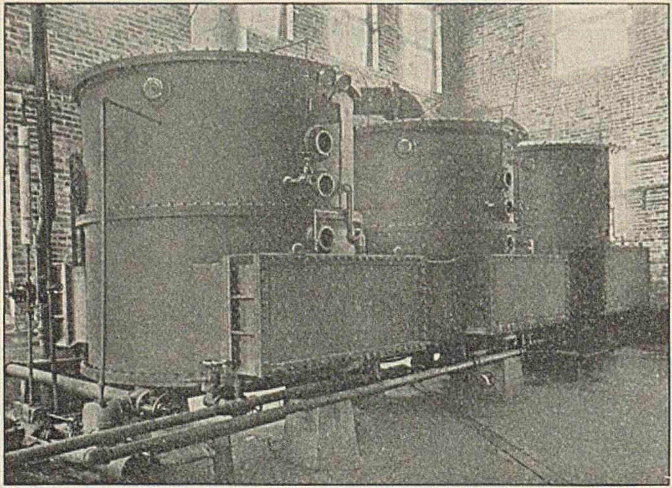

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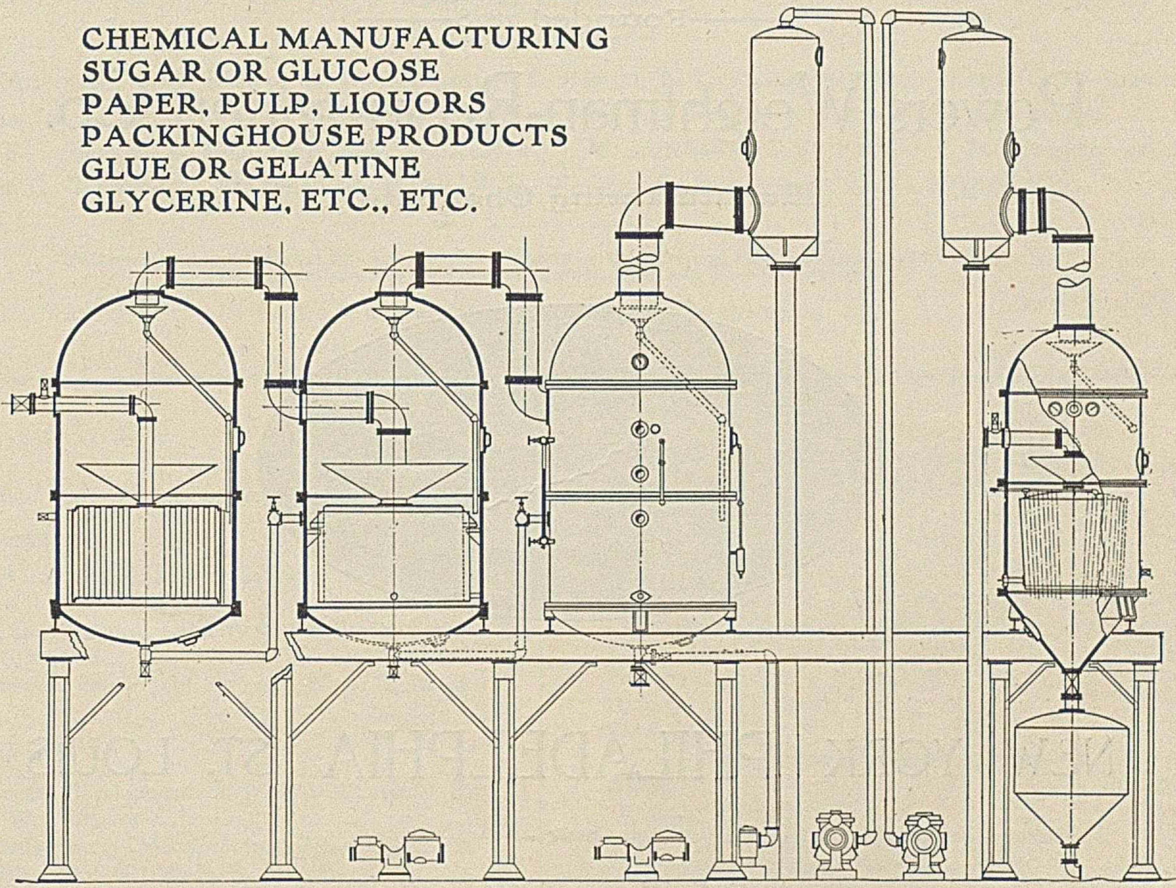

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