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EDITORIALS

EDUCATION FOR RESEARCH[1]

The general disturbance in the chemical and pharmaceutical market occasioned by the present European war has sharply emphasized the dependence of many American industries upon the supply of both raw and finished material obtained from abroad. The public is asking the pertinent questions: Why must we import so large a proportion of our coal tar dye stuffs, when we have so much highly colored coal tar at home? Why do we depend upon Germany for lithia salts, when all the lithium-bearing minerals come from America? Why has a European war increased the price of articles not in any way connected with the war?

It is a principle of pedagogy that, to insure the best results when giving instruction, it is necessary to create a receptive attitude on the part of the student; to encourage an inquiring frame of mind. Today there is a keener and broader interest among manufacturers than ever before in determining those factors which have been controlling in giving European nations an advantage in many lines of industry which it would seem the United States is in every way equally fitted to enjoy. The public now possesses that desirable receptive attitude and inquiring frame of mind. It would seem therefore that the present is a psychological moment for a campaign of education which would benefit the chemical profession directly, and the entire community indirectly.

A number of very important factors in successful chemical industry have already been considered by this audience and your able committee has reported its findings and recommendations regarding a so-called anti-dumping clause, an adequate protective tariff and the United States patent law. There are, however, some very general matters bearing upon the subject that may be profitably considered. First, there is the necessity for further education of the public. Notwithstanding all that has thus far been done, the public is, as a whole, ignorant of what a chemist professionally is, and the place he occupies in the community. A great many people do not yet distinguish between a chemist and an apothecary, or between the latter and a dispenser of soda water. A chemical engineer is frequently visualized as a man who runs a so-called chemical fire engine. And yet this same public will talk volubly about the position occupied by Germany in the industrial chemical world and ascribe untold advantages to systems of education and industry which it does not understand. The magnificence of German chemical industry has been compared to the chemical industry of America almost *ad nauseum*. Generally the inequalities are greatly exaggerated and many may be explained without any discredit to the American profession. We are wont to instance the telegraph, the sewing machine, the electric light and such developments, when desiring to find compensating achievements to offset the contributions of Germany to chemical science. But we forget that the sulfite process for obtaining cellulose from wood, the chromium process for leather, calcium carbide, carborundum, and many other chemical industries owe their origin and development to American chemical genius. Nothing succeeds like success; and while we should continue to learn from Germany the many things which she is in position to teach us, we must cease making unfair comparisons and root for the home team.

The increasing appreciation with which the chemically trained man is held by the American manufacturer argues well for the future. Not many years ago if a chemist was employed at all, it was simply and only for so-called control work. The manufacturer was satisfied if he maintained his standard, and turned out a uniform product. There was little inclination to risk money by placing on the market a new product. There has been an encouraging change within the last ten years, and the manufacturing public is awakening to the desirability of progress in both the quality of his product and the methods of his plant; and he is beginning to realize that a man trained in experimental science is a necessary addition to his organization. But the average manufacturer of America still expects bricks without straw. To cite an example of what I mean: A large shoe machinery company known to us thinks nothing of allowing a skilled mechanic two or three years in which to perfect a desired movement or correlation of parts in a machine. Yet this same company was keenly disappointed, even disgusted, because a skilled chemist did not produce in six weeks a special alloy with sharply defined properties. In one case the solution depended upon mechanics which the superintendent understood and could see, while in the other it was chemistry which he did not understand and the action of which he could not follow.

The manufacturer of today is beginning to be strongly attracted by the terms "research" and "research department." He has a sort of conviction that, by adding such an appendage to his organization, he will be insured of progress and will protect himself from difficulties, much in the same way that a good vaccination mark insures against small-pox.

My plea at this time is not so much for greater generosity on the part of the employer in matters of laboratory facilities, special equipment, or a good library, however inportant these are, but rather for a larger appreciation of the conditions which make for ultimate success in research work. Among these conditions may be mentioned, first, the choice of the research worker. I am satisfied that no little harm is done the cause of industrial research by the employment of immature, untrained men, who pass as men skilled in science but who either know no science, or who have had no experience in that very difficult art of applying science to industry. The harm comes not so much because the particular investigation fails, but rather because the

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[1] Address at the Joint Meeting of the New York Sections of the American Chemical Society, the Society of Chemical Industry and the American Electrochemical Society, Chemists' Club, December 11, 1914.

management believes it has shown that its problems are not susceptible to solution by scientific research or amenable to the aid which applied science can render. This unfortunate condition is frequently brought about by false economy on the part of the management. A research chemist should in its opinion be obtained with the ease and salary of an apothecary's clerk. A horse suitable for drawing an ice cart is bought and expected to win a Derby.

Another mistake frequently made is in the organization of the research staff, or if done on a less pretentious scale, the research work. Investigation work should never be allowed to interfere with factory production. The average mill superintendent quickly becomes antagonistic to anything which cuts down his output. Yet it is not infrequently the case that a research assistant is placed directly under such a superintendent, and may even report to him exclusively. The superintendent may have won his position on account of his ability to get the maximum of work out of his men, and may have risen in spite of an extreme narrowness of vision, rather than on account of his breadth of view. Or again, the research man may be at the beck and call of the production department and thus be constantly taken away from his real task to do routine testing of the product; or, the purchasing department may have the right to demand such of his time as may be necessary to check up specifications, and purchases made thereunder. Continuous concentrated effort is essential to a successful investigation, and the organization of such work should insure freedom from serious interruption of any kind.

A further tendency on the part of the employer is to expect positive results as soon as the work is well under way; having planted the seed he is impatient to harvest the crop. At best, experimental work is slow and this fact must be cheerfully accepted at the beginning. When considering the large amount of research work done in Germany we forget the great number of men who are there engaged in investigations of every possible type. If we had some means of determining the average yearly output per man, I am sure we would find it extremely small. It is my belief that the *per capita* return for research work is greater in America than it is in Germany. It is only when the results of each individual are multiplied by the great number of men in the work that the enviable amount of scientific work produced yearly in Germany is reached.

As a transition paragraph from the employer to the employee, I shall again emphasize the point already treated elsewhere. For the best results a manufacturer should realize that his organization must teach the college man the details of the work for which he is employed; and the new graduate must realize that there is an enormous lot which he does not yet know, and which the factory superintendent or foreman can best teach him. Fault is frequently found with the college man because he does not know the latest quick analytical methods as used in some large laboratory; that he is not familiar with the types of machines employed in the factory to which he goes. Inasmuch as the average candidate has but four years for his technical training it follows that if he had been taught these details upon which his *immediate* success may possibly depend, it would have been at the expense of a broad, fundamental training in economics and science upon which his final success is sure to depend. On the other hand there is much truth in the oft-repeated assertion that the college graduate "thinks he knows it all." He fails to realize that in every industry there is a great field of knowledge of which he is as yet ignorant but which is familiar to the manager, superintendent or foreman. Not only the details of factory procedure, but matters of finance, salesmanship, advertising and other factors essential to the success of the undertaking are unknown to him.

Finally we come to the education of the man who is to do the research work. At this time it would be out of place to discuss curriculums of study or to outline courses of instruction; but there are two or three points which it may be worth while to consider.

In general it may be said that a man should possess the ability to utilize the knowledge he has acquired in the past in the solution of his present problems. This statement presupposes two things: *first*, the acquisition of knowledge, and *second*, a training in the application or use of this knowledge. Comparatively speaking, the first is easy and the second is difficult. In a limited sense, knowledge can be bought in the form of books, but no one can appropriate to himself a skilled hand or an observant eye or an accurate analytical mind. These are the products of training. There is a regrettable tendency in modern textbooks on elementary chemistry and qualitative analysis to spend an undue amount of time upon the laws of dilute solutions to the exclusion of that training which these subjects are preeminently fitted to give. Not that these laws are of little importance; but fundamental principles and broad generalizations are of value only when they can be visualized in terms of facts and experiences. But the present tendency to overemphasize theory in elementary chemistry and qualitative analysis crowds out that knowledge of facts, and training in observation, in which the beginner is so deficient. The great difficulty with the average student in experimental science is that he sees things as he thinks they ought to be, and not as they are. He does not observe accurately, nor reason logically. He is not resourceful in using the knowledge acquired yesterday in solving the problems of today. Such power can be obtained only by practice; and why postpone the practice of this all-important function until late in the college course? From my experience as a teacher it is my opinion that no subject in the entire curriculum is so well adapted to train a man in keen observation, logical deduction and general resourcefulness, as a broad and sympathetic course in qualitative analysis. The short time usually devoted to this subject should not be consumed in teaching advanced theory which can be better learned later.

A second factor in the education of a research man (but which of course is not limited to a research man) is the necessity of giving him a working knowledge of the general principles of chemistry in the same manner that a mechanical engineer is made familiar with those principles of physics involved in thermodynamics and applied mechanics. So I use the word *working* advisedly, and mean thereby not only a knowledge of the fundamental theories and laws involved in every-day phenomena, but an acquaintance with them intimate enough to enable him to make daily use of them. The average student knows well the law of conservation of energy and of mass; although his arithmetic is usually poor, the law of multiple proportions is second nature to him and he handles it with ease. This is because the law is valid at all workable concentrations, at all workable pressures, and at all workable temperatures; and he has met with problems for the solution of which its application is imperative. Not so with the laws which he meets later in his work. In his course in Theoretical Chemistry or Physical Chemistry or General Principles of Science, or whatever name it may be called, he learns, for example, the law of mass action; if he solves any problems at all, they involve dilute solutions or low pressures alone. He learns that for concentrated solutions and strongly dissociated salts the law does not hold—and there the matter rests. He learns Henry's law, Raoult's law, the law of electrolytic conductance, transference, osmotic pressure etc., and if the subject is well presented, solves numerical problems to render clear his mental image of these laws; then he learns that under those conditions in which he lives and moves and has his being, they do not quantitatively hold—and there matter rests.

Imparting to the student a knowledge of these general laws of science is one of the most important factors in technical education and must play a leading part in the upper year of college work. But the point I would emphasize is that when these principles are presented, the task is only begun. The first instruction must of necessity be given, set as it were, in dilute solutions. To be of pedagogic value, the work must be quantitative, and accuracy can be realized only in very low concentrations. But here is where the average teacher of so-called theoretical chemistry "lies down on the job." To have a working knowledge of these principles a man must be familiar with their use under the conditions of concentration, temperature and pressure with which he has to deal. He must have a general idea of the deviation from the theoretical which a law will suffer under working conditions. If such laws are not quantitatively applicable, they are at least qualitatively helpful; if they do not determine how far one can go to reach a definite end, they at least indicate the direction he must go. Our experience with men who have had a course in the general principles of chemistry is that they do one of two things—either they attempt to use the knowledge thus obtained, and develop a confidence in their ability to get at the roots of the problem and by applying these general principles determine the lines along which success most probably lies; or to use an analogy, they are afraid to venture into the open ocean of practical experience with a boat which they have sailed only in the closed and secluded harbor of dilute solutions. The result is that they lose interest in the boat and soon entirely forget her. Had they been taught to navigate this boat in times of storm and high tides as well as in the harbor, they might not have attained on the ocean the accurate time they were accustomed to make in the harbor, but they would the more quickly have reached the haven of success which lies on the opposite coast.

It is but a truism to say that the way to acquire an ability to solve problems is in the exercise of this faculty. To become a successful research worker, we must do research work. While in every institution an attempt is made to train students to carry on original work, the four years allotted to the average man are not sufficient for accomplishing very much in this direction. While a genius is born, not made, good experimentalists can be produced from most men of average ability.

It is believed that the training to be obtained from investigation work is largely independent of the particular type of problem undertaken. If one wishes to become a bridge builder by the experience of building bridges, it is not material whether the bridge so built is demanded by the traveling public or not. It is in solving the problems incident to construction, not in the use of the finished structure, that the educational value lies. Thus it is with research work in so-called pure and applied science—whether the results obtained be immediately used, or very remotely used, need not influence the methods employed in the work.

So, in research laboratories, bridges are built not only where the public is anxious to have them built, but where someone is willing to pay for the building. The problems undertaken are brought by manufacturing concerns, and the expenses of the laboratories are met in this way. A two-fold purpose is thus accomplished—the manufacturing public is given facilities for overcoming some of its difficulties, and the more able men of the community are trained to fill the demand, which is constantly growing and now far outmeasures the supply, for men capable of conducting successful original research.

William H. Walker

CHANGES IN THE EDITORIAL STAFF OF CHEMICAL ABSTRACTS

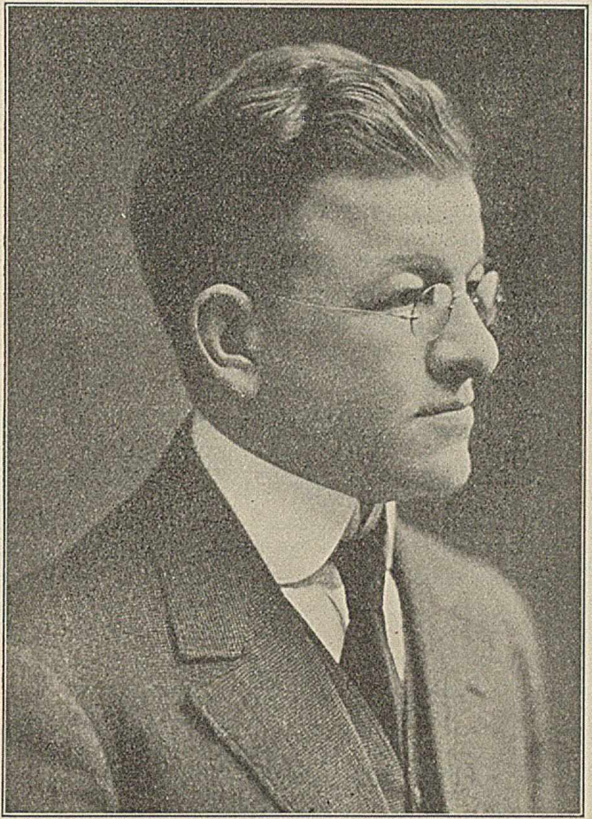
The resignation of John J. Miller, Editor of *Chemical Abstracts*, to accept a managerial position, seems an appropriate occasion for an appreciation of his services to the Society.

Mr. Miller entered the work five years ago as Associate Editor, during which time the scope of the publication and the labors of the editorial force have grown greatly. Although Mr. Miller has been editor only six months, he had for the previous three years carried a large and increasing amount of editorial responsibility. His editorship was well earned and it is a matter of great regret to us that the Society must lose him.

Mr. Miller's special contribution to the Society's enterprise was executive ability of a high order and an energy that more than kept pace with the growing task. In the early years of the journal the editors used to wonder how the management of the *Zentral-*

blatt ever succeeded in publishing their semi-annual index with the last copy. Last year, however, the members of our Society received the much larger *Chemical Abstracts* index before the end of the calendar year. This result was not attained without a systematic improvement from year to year, but that it was achieved at all is due largely to Mr. Miller, assisted by Mr. Crane, and by Miss Laura Collison, who indexes *Abstracts* and the *Journal of our Society* so efficiently. Mr. Miller strove continually to extend the usefulness of *Abstracts* in many other ways, with notable success.

Mr. E. J. Crane, who now becomes Acting Editor, joined the office force as second associate editor something over three years ago. He is a young man of much ability, and naturally suited to editorial work. The writer feels that the Society is to be congratulated in having developed such men as these. A few years ago there was hardly such a thing as a paid chemical editorial position in this country. Now there are a few, and the number is sure to increase as the literature of the science becomes larger and larger. Is it not much better to discover the men that are naturally adapted to this work, train and promote them, than to select men because they have distinguished themselves in some other way in chemistry? For this reason it is a hopeful sign that the principle of promotion is being applied in the office of *Chemical Abstracts;* the Society will thus be best served and a better class of men can be secured to fill the subordinate positions.



JOHN J. MILLER

AUSTIN M. PATTERSON

THE ANNUAL MEETING OF THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS

The program of the last meeting of the American Society of Mechanical Engineers contained much material of direct interest to industrial chemists.

One day was devoted, under the direction of the Committee on Public Relations, to a consideration of the engineering questions involved in municipal administration. The purpose of this discussion was to direct the attention of good engineers to municipal opportunities and to get politicians, investigators and reformers to recognize and adopt engineering methods which are constructive instead of destructive, and which are based on facts rather than on opinions.

Another feature of the meeting was the formulation of a standard law for the regulation, construction, operation and inspection of steam boilers and other large pressure vessels, in the interests of public safety. This law was formulated to serve as a model for use by the different state legislatures and thus aid in unifying the existing laws. Many states now have either no laws at all or very bad ones. The present laws of some states even permit them to become the dumping ground for discarded boilers from other states.

The human element, the key to economic problems, was the subject of the presidential address by James Hartness. Mr. Hartness pointed out that the world of mechanism has become so intricate and complex that it has gone beyond the capacity of any single individual; that each person must be content to comprehend only a small part, and that it is only by selecting the character and limiting the amount of material taken into individual minds that the best results can be accomplished. Carrying the principles of the individual into the realm of organized industry, he points out that large organizations are essential as affording the opportunity for the most complete subdivision of work and the greatest degree of specialization, both of which lead to the most efficient employment of human energy. A most important element therefore in a large manufacturing plant is its organization. Without this the buildings and equipment are of little value. The greatest good to the greatest number requires taking into consideration each human being, his desires and his needs in finding the work for which he is best endowed.

President Hartness recommends that in addition to the regular treasurer's report, each industrial unit should have a human report, beginning with a description of the directors and going through the entire organization. It should contain a statement regarding the elements of harmony of the organization, the length of service of manager and workers, frequency of change of methods or articles manufactured, intelligence of executives in the management of men, the degree of contentment of each member, the extent to which each man in the organization approaches the best position for which he is endowed, how nearly he obtains the best remuneration for which he is qualified, the extent to which the management recognizes the inertia of habit of both mind and body, the degree in which the various men in the organization approximate the condition of highest efficiency, the extent to which the management goes in the expression of appreciation, the degree of its knowledge of the most important characteristics of man as indicated by his inner motives and desires and the condition of his mind as he goes to his home. Finally, all of these elements should be carefully appraised and the average should be the rating of the company. Mr. Hartness thinks that an investor, considering this human rating along with the treasurer's statement, would seldom make a mistake in estimating the true worth of an industrial organization.

ORIGINAL PAPERS

PHYSICAL PROPERTIES OF THE METAL COBALT[1]

By Herbert T. Kalmus and C. Harper

Received October 1, 1914

This paper is the third of a series describing investigations of the metal cobalt and its alloys. It is a report on a large number of measurements made at this laboratory of some of the important physical and mechanical properties of metallic cobalt. The properties which have been particularly studied are:

1—Density
2—Hardness
3—Melting Point
4—Tensile Strength
5—Compressive Strength
6—Rolling and Turning Properties
7—Electrical Resistance
8—Magnetic Permeability
9—Specific Heat

PREPARATION OF METALLIC COBALT FOR THE STUDY OF ITS PHYSICAL PROPERTIES

It is true of cobalt, as of most metals, that its physical properties are often greatly influenced by the presence of small percentages of impurities. It is well known, for example, that less than 0.01 per cent of arsenic in copper is sufficient to account for a drop in its electrical conductivity[2] of 3.3 per cent. Similarly, for cobalt we find that a few tenths of a per cent of impurities often doubles or trebles its electrical resistance (see Tables VI and VII).

Table I—Density of Cobalt

All samples were cast from just above melting point in an iron mould and allowed to cool in the mould
Except in cases noted, all samples were then turned in the lathe to their final form

Sample No.	Analysis				Date	Form of sample	Special treatment	Density		
								Value	at °C.[2]	
"Commercial Cobalt"—Unannealed										
H 109	Co 96.8 Ni 0.56	Fe 2.36 C 0.063	S 0.022 P 0.017		Dec. 8, 1913	Cylindrical bar	None	8.7997	18.5	See Fig. IX
H 130	Co 96.5 Ni 2.0	Fe 1.27 C 0.305	S 0.054 P 0.015		Feb., 1914 Average of 5	Thin cylindrical bar	None	8.7690	17.0	See Fig. IV
H 87*c*	Co 97.8 Ni 0.5	Fe 1.46 C 0.18	S 0.02 P Trace	Si 0.02 Ca Trace	Feb., 1914 Average of 4	Cylindrical bar	None	8.6658	17.0	See Fig. VIII
Pure Cobalt—Unannealed										
H 212	Co 99.9 Ni None	Fe 0.20 C None	S 0.017	Si None Ca None	Jan.-Feb., 1914 Average of 6	Cylindrical bar	None	8.7562	17.0	See Fig. I
H 214	Co 98.71 Ni None	Fe 1.15 C 0.039	S 0.012 P 0.010	Si 0.14 Ca None	Apr. 3, 1914	Wire of 0.0901 cm. diam.	Swaged, see p. 11	8.8490	15.0	See Fig. I II
H 193	Co 99.1 Ni None	Fe 0.80	S 0.021	Ca Trace	Nov. 15, 1913	Cylindrical bar	None	8.7889	20.0	
H 213	Co 99.73 Ni None	Fe 0.14 C None	S 0.019	Si 0.02	Jan.-Feb., 1914 Average of 3	Cylindrical bar	None	8.7732	16.0	See Fig. II
Pure Cobalt—Annealed										
H 212	Co 99.9 Ni None	Fe 0.20 C None	S 0.017	Si None Ca None	Jan. 12, 1914 from 700° C.	Thin cylindrical bar	Annealed from 700° C.	8.8105	14.5	
Pure Cobalt—Rolled										
H 213	Co 99.73 Ni None	Fe 0.14 C None	S 0.019	Si 0.02	Jan. 19, 1914	Thin cylindrical bar	Swaged	8.9278	14.0	
H 212	Co 99.9 Ni None	Fe 0.20 C None	S 0.017	Si None Ca None	Jan. 23, 1914	Wire of 0.0840 cm. diam.	Swaged	8.9227	19.0	

The cobalt for these investigations has been prepared by reduction of cobalt oxide, Co_3O_4. Commercial oxide was obtained from the smelters, and after a crude purification, was reduced to form what we shall call "commercial cobalt;" also the commercial oxide was purified to a high degree, from which has been prepared what we style "pure cobalt." These two names are used in this paper largely for brevity and convenience; the analysis of each sample is given with the data of its properties. The properties of each of these have been measured and will be discussed separately.

The methods of preparation of the pure and commercial cobalt used in these researches are given in the original paper, and outlined in "Preparation of Metallic Cobalt by Reduction of the Oxide."[1]

COLOR—Pure metallic cobalt very much resembles nickel in color, although, when plated and polished under proper conditions, while beautifully white, it possesses a slightly bluish cast. Sometimes it deposits as a black matte. Metallic cobalt which has been reduced from the oxide at a sufficiently low temperature is a gray powder.

I—DENSITY (SPECIFIC GRAVITY)

The densities of both cast and rolled cobalt were determined in this laboratory by the Archimedes method. A sphere or cylinder of the material was weighed, using a delicate balance, both in air and under water. In the computations the weighings were corrected for the buoyancy of the air, and the measurements reduced so as to be expressed in terms of water at its maximum density. Table I gives the results.

A number of density determinations of metallic cobalt, as made by other investigators, are recorded in the literature, most of which, however, were made at an early date, and very little is said of the nature of the metal. The following table of values is taken

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[1] Authors' abstract of report under the above title to the Canadian Department of Mines. Published by permission of the Director of Mines, Ottawa, Canada. This publication is one of a series on the general investigations of the metal cobalt and its alloys, with reference to finding increased commercial usages for them. These are being conducted at the School of Mining, Queen's University, Kingston, Ontario, for the Mines Branch, Canadian Department of Mines. See This Journal, **6** (1914), 107 and 115.

[2] J. H. Dellinger, "The Temperature Coefficient of Resistance of Copper," U. S. Bureau of Standards, *Bull.* **7** (1911), 79.

[1] This Journal, **6** (1914), 107; *Bull.* **259**, Mines Branch, Dept. of Mines, Ottawa, Canada.

from the more recent and probably more accurate of them:

DENSITY OF COBALT

Other workers			Kalmus and Harper		
Tilden(*a*).........	8.718	21° C.	Unannealed	8.7918	17.0° C.
G. Neumann and F. Strenintz(*b*)..	8.6	...	Annealed	8.8105	14.5° C.
Copaux(*c*)........	8.8	15° C.			
Winkler(*d*).......	7.9678	...	Swaged	8.9253	16.5° C.

(*a*) *Chemical News*, **78** (1898), 16.
(*b*) *Monatshefte für Chemie*, Vienna, **12** (1891), 642.
(*c*) *Annalen de Chimie et de Physique*, [8] **6** (1905), 508.
(*d*) *Berg und hüttenmännische Zeitung*, **39** (1880), 87.

The values from the literature are generally lower than those measured by us, no doubt because of impurities in the metal, or because of the difficulties of casting without occluding a certain amount of gas.

2—HARDNESS

Hardness measurements were made in this laboratory on a standard Olsen hardness testing machine of 100,000 lbs. capacity. (Tinius Olsen Co., Philadelphia, Pa.) The machine consists of a framework on which is mounted a lever system. To one end of this lever system a penetrating ball is attached, while at the other, weights are attached, which, when applied, cause motion of the lever system and penetration of the ball into the metal to be tested. An instrument is mounted on the main lever which measures automatically the actual penetration of the steel ball to 0.0001 of an inch.

TABLE II—BRINELL HARDNESS OF COBALT
All samples were cast from just above melting point, allowed to cool in iron mould and turned in lathe
Special treatments beyond this are noted below. Load 3500 lbs. unless given otherwise

Sample No.	Analysis			Date	Special treatment	Brinell hardness	Remarks
"COMMERCIAL COBALT"							
H 109	C 0.062	S 0.022	P 0.017	12/ 9/1913	None	111.4	See Fig. IX Metal soft, tough and turns with medium long curling chip
				1/14/1914	None	100.9	
				12/11/1913	None	104.4	
				12/22/1913	None	111.7	
				9/15/1914	None	100.2	
H 214*c*	Co 97.09	Fe 1.45	Si 0.011	9/15/1914	Annealed from 850° C.	138.6	See Fig. V
	Ni None	C 0.067	P 0.010	9/15/1914	Annealed from 1000° C.		
	Mn 2.04	S 0.012	Ca None			136.9	See Fig. VI
	Co 98.7	Fe 1.15	Si 0.14	9/15/1914	None	123.9	See Fig. III
	Ni None	C None	P 0.011				
		S 0.012	Ca None				
H 211	C 0.10			1/14/1914	None	128.2	Metal soft and medium tough. Machines with long curling chip. See Fig. X
				9/15/1914	None	130.7	
H 87*c*	C 0.13	S 0.022	P 0.012	1/16/1914	None	131.0	Metal medium hard and tough. Machines with curling chip. See Fig. VIII
H 87*a* and *e*	C 0.22	S 0.03	P None	12/22/1913	None	119.2	
				9/15/1914	Quenched from 1200° C.	132.9	
H 130	C 0.305	S 0.054	P 0.015	12/11/1913	Quenched from 1200° C.	115.0	Metal short grained, brittle and turns with short chip
				9/15/1914	Quenched from 1200° C.	113.8	
				1/14/1914	None	116.6	Metal soft and tough. Machines with curling chip. See Fig. IV
H 87*d* and *b*	C 0.36	S 0.016	P None	2/ 1/1913	None	112	Very tough to turn in lathe
	C 0.37	S 0.015	P None	2/ 1/1913	None	117	
PURE COBALT							
H 193	Co 99.1	Fe 0.80	S 0.02	11/15/1913	None	129.7	Load 2500 lbs. Metal soft and brittle. Machines with short chip
	Ni None	C None	Ca Trace				
				12/ 9/1913	None	133.4	
				11/15/1913	None	131.2	
H 212	Co 9.99	Fe 0.20	S 0.017	1/ 9/1914	None	105.5	Load 2500 lbs.
	Ni None	C None					
				1/14/1914	None	128.7	Metal soft and brittle. Machines with short chip. See Fig. I
				1/14/1914	Annealed from 700° C.	130.8	Load 2500 lbs.
H 213	Co 99.73	Fe 0.14	S 0.019	1/14/1914	Annealed from 700° C.	121.0	Metal soft and brittle. Machines with short chip See Fig. II
	Ni None	C None					
H 217	Co 99.55			9/15/1914	Annealed two hours at 600° C., allowed to cool slowly, and again turned in lathe	125.9	
				9/15/1914	None	109.5	

All hardness measurements of the metal cobalt made by us have been computed in the Brinell system, and have been made with a sphere of one centimeter diameter, and with a load of 3500 pounds, unless stated otherwise.

We have measured the Brinell hardness of a series of common substances under the identical conditions that we have used for cobalt, and a table of these values is given below for comparison. In each instance the value is the mean of a number of observations, and they are reproducible, on the same sample, to within a few per cent. Different samples of most of these materials give values differing considerably among themselves. This table is given merely to serve as a rough basis of comparison.

COMPARISON TABLE OF BRINELL HARDNESS

	Load Lbs.	Brinell Hardness	Load, 3500 lbs.	Brinell Hardness
COPPER............	1000	65.6	MILD STEEL.............	109.9
Rolled...........	1000	67.4	Cold rolled shafting.....	126.2
Sheet............	3500	75.0	TOOL STEEL.............	153.8
Unannealed.......	3500	81.9	"Crescent"...........	130.2
SWEDISH IRON......	3500	90.7	SPRING STEEL...........	160.3
	1000	68.6		178.0
			TOOL STEEL	
	3500	75.2	SELF HARDENING	180.0
WROUGHT IRON.....	3500	92.0	"Rex," before hardening	162.1
	1000	83.1	"Rex," after hardening.	240.0
	3500	100.2		
CAST IRON.........	3500	97.8	Self hardening from School of Mining Workshop....	259.0
	1000	84.4		
	3500	104.5		

COBALT FOR BRINELL HARDNESS MEASUREMENTS—The hardness of cobalt, like that of most other metals, is determined to a greater extent by its physical and mechanical treatment than by slight variations in its chemical composition, if we except the presence of carbon. Even our "commercial cobalt" contains but small percentages of total impurities of which the greater part is iron and nickel, and which, in the small amounts present, would not greatly affect the hardness.

Table II reports the hardness measurements made. In the samples under "commercial cobalt" the percentage of carbon is given throughout, and the other impurities are between the following limits:

S........	0.010 to 0.070 per cent	Fe......	0.10 to 1.0 per cent
Ca......	Trace to 0.015 per cent	Ni......	Trace to 0.50 per cent
Si.......	Trace to 0.20 per cent	C.......	0.10 to 0.60 per cent

The total impurities in any one sample of this "commercial cobalt" rarely exceeded 1.5 per cent.

BRINELL HARDNESS MEASUREMENT—A single measurement of the Brinell hardness is given in full to show the concordance of observations among themselves, and the details of computation. This may be taken as typical of the large number of measurements which were made.

Sample H 193 Initial reading	Dec. 9, 1913 Reading under load	Load, 3500 Lbs. Indentation (in.)
0.0344	0.0489	0.0145
0.0333	0.0480	0.0147
0.0309	0.0465	0.0156
0.0321	0.0468	0.0147
		Average, 0.0149 in. = 0.379 mm.

$$\text{Brinell hardness by definition} = \frac{\text{total pressure in kg.}}{\text{area of depression in mm.}^2} = \frac{P}{2\pi rh}$$

where, P = Load in kg.
r = radius of indenting ball in mm.
h = depth of depression in mm.

$$\therefore \text{Brinell hardness} = \frac{3500}{2.2} \times \frac{1}{2 \times \pi \times 5 \times 0.379} = 133.4$$

HARDNESS OF COBALT AS OBSERVED BY OTHER INVESTIGATORS—There is very little in the literature on the hardness of cobalt, except a few more or less qualitative observations. However, a careful measurement seems to have been made by R. Reur and K. Kaneko,[1] from which they compute the Brinell hardness of cobalt to be 132.

COMPARATIVE HARDNESS OF NICKEL AND COBALT—For comparison we have measured the hardness of both cast and sheet nickel under the same conditions that we have used for cobalt, load 3500 lbs., and found them to be, respectively, 83.1 and 85.1 Brinell, the latter for a 1/4 inch sheet. An independent check test on the hardness of cast nickel gave as a result 76.4.

CONCLUSIONS—HARDNESS

I—Table II shows the Brinell hardness of cobalt cast from just above the melting point, and allowed to cool in an iron mould, to be in the neighborhood of 124.0 (load 3500 lbs.). This is the mean of nine observations with an average deviation from the mean of 7.9.

II—The hardness of cobalt cast from just above its melting point is considerably greater than that of either iron or nickel, under corresponding conditions.

III—The effect of the addition of 0.060 to 0.37 per cent of carbon on the hardness of "Commercial" cobalt is not sufficient to offset the effect of slight variations in heat treatment. The measurements are not sufficiently concordant to warrant drawing general conclusions.

3—MELTING TEMPERATURE OF COBALT

A considerable number of melting point determinations of the metal cobalt were made in an Arsem electric vacuum furnace (General Electric Company, Schenectady, N. Y.). These determinations were carried out by the usual cooling or melting curve method, using pure alumina crucibles and alundum lined graphite crucibles.

Cobalt has a very sharp melting point, differing in this respect from iron, which becomes plastic as it approaches its melting point. With iron the actual temperature of melting is not sharply defined, there being a considerable transition region, whereas with cobalt quite the reverse is true. Therefore, the melting point of cobalt may be determined with accuracy by the cooling and melting curve method.

TEMPERATURE MEASUREMENTS—Temperature observations were made with a Wanner optical pyrometer, which was checked against an amyl acetate lamp standard before and after each set of runs, in accordance with a calibration certificate from the Physikalisch-Technische Reichsanstalt, at Charlottenburg. This pyrometer was also used to measure the melting points of copper and nickel during the period of its use for the determinations on cobalt, which measurements agreed with the calibration curve used to within a few degrees. For this work the melting point of nickel was considered to be 1444° C., and of copper to be 1084° C.

The melting point of nickel, considering our calibration curve from the Reichsanstalt to be correct, was determined six times as follows:

° C.	Deviation from the mean
1438	6
1437	7
1445	1
1446	2
1448	4
1450	6
1444 Mean	4.3° C. Average

The nickel (see Fig. XI) used for these melting point measurements analyzed as follows:

Ni...............	99.29	Ca.......	None
Fe...............	0.48	C........	None
S................	0.025	Co.......	None
Si...............	0.042	Total,	99.84 per cent

The cobalt (Sample No. 212—see Fig. I) used for these melting point determinations analyzed as follows:

Co...............	99.9	Ca.......	None
Ni...............	None	Si........	None
Fe...............	0.20	C........	None
S................	0.017	Total,	100.12 per cent

Table III—Summary of Results of Melting Point Determinations

Date of run	Determined melting point of cobalt	Deviation of single observation from the mean
Sept. 27, 1912	1474° C.	7
Sept. 30, 1912	1472	5
Sept. 30, 1912	1472	5
Oct. 1, 1912	1470	3
Oct. 1, 1912	1472	5
Jan. 13, 1914	1467	0
Jan. 13, 1914	1467	0
Jan. 14, 1914	1460	7
Jan. 15, 1914	1453	14
Jan. 15, 1914	1468	1
Jan. 15, 1914	1468	1
Jan. 19, 1914	1462	5
Jan. 19, 1914	1460	7
Jan. 19, 1914	1470	3
Jan. 19, 1914	1462	5
Jan. 19, 1914	1470	3
Mean melting temperature,	1467° C.	Average, 4.4° C.

From these observations the melting point of pure cobalt would appear to be 1467° C. ± 1.1° C. [Note, however, conclusions below, second paragraph.]

It should be noted that Burgess and Waltenberg[1] use the value 1452° C. as the melting temperature of nickel. If we adopt this value instead of 1444° C. (see below), our value for the melting temperature of cobalt would be practically identical with theirs, namely, 1478° C.

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[1] *Ferrum*, **10**, 257; *Chem. Abs.*, **1913**, p. 3591.

[1] United States Bureau of Standards, *Bull.* **10** (1913), 6.

THE MELTING POINT OF COBALT AS DETERMINED BY OTHER INVESTIGATORS

INVESTIGATOR	Melting temperature	Purity Per cent	Method of measurement
Burgess and Waltenberg(*a*)	1477° C.	99.95	Micropyrometer
Burgess and Waltenberg(*a*)	1478° C.	99.95	Crucible melts in electric furnace
G. K. Burgess(*b*)	1464° C.	Very pure	Micropyrometer
H. Copaux(*c*)	1530	Not given	Interpolation between gold and platinum points
Guertler and Tamman(*d*)	1528	98.3 Rest largely Ni and Fe	Cooling curve
Guertler and Tamman(*e*)	1468	98.3	Cooling curve
Guertler and Tamman(*f*)	1505	98.3	Cooling curve
Guertler and Tamman (*e*)	1455	98.3	Cooling curve
R. Ruer and K. Kaneko(*g*)	1491	..	....

(*a*) Bureau of Standards, *Bull.* **9** (1912), 475; *Bull.* **10** (1913), 13.

(*b*) *Ibid., Bull.* **3** (1906), 350.

(*c*) *Annalen de Chimie et de Physique,* [8] **6** (1905), 508.

(*d*) *Zeitschrift für anorganische Chemie,* **42** (1904), 353.

(*e*) Their value corrected for melting point of nickel = 1451 instead of 1484 as taken by them.

(*f*) *Zeitschrift für anorganische Chemie,* **45** (1905), 223.

(*g*) *Ferrum,* **11** (1913), 33–9.

CONCLUSIONS—MELTING TEMPERATURE

The melting temperature of cobalt, as determined by us, is 1467 ∓ 1.1° C. This is for metal 99.9 per cent pure, and is the mean of 16 determinations by the cooling and heating curve method.

This value of the melting temperature is based upon pyrometer calibration curves, considering the value of the melting temperature of nickel to be 1444° C. If we adopt the more probable value 1452° C., for the melting temperature of nickel, **our melting temperature for cobalt is 1478° C. ± 1.1° C.**

4—TENSILE STRENGTH MEASUREMENTS

The tensile strength tests were made on a Riehle universal standard vertical screw power testing machine (Riehle Testing Machine Co., Philadelphia, Pa.), of 100,000 lbs. capacity, operated by direct connection to an electric motor.

TEST BARS—All bars for tensile strength measurements have been "Proportional Bars," as recommended and adopted by the International Association for Testing Materials.

Table IV reports the data for our measurements on "commercial cobalt" and on pure cobalt.

There is almost no literature on the tensile strength of cobalt, although Copaux[1] gives—cobalt 69,000 lbs per sq. in., nickel 58,000 lbs. per sq. in.

We measured the tensile strength of pure iron and pure nickel at this laboratory, under conditions similar

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[1] *Annalen de Chimie et de Physique,* [8] **6** (1905), 508.

TABLE IV—TENSILE STRENGTH MEASUREMENTS OF COBALT

All samples (except wires) were cast from just above melting point in an iron mould and allowed to cool in the mould
Special treatments beyond this are noted below

Sample No.	Analysis	Date	Special treatment	Lbs. per Sq. In.		Percentage		Remarks
				Tensile breaking load	Yield point	Reduction in area	Elongation in 2 in.	
"COMMERCIAL COBALT"—Unannealed								
H 109	Co 96.8 Fe 2.36 S 0.022 Ni 0.56 C 0.062 P 0.017 Si None Ca None	12/ 9/1913	None	48,700	33,800	7.7	5.5	Fairly fine-grained fracture
		12/ 9/1913	None	52,800	33,800	8.7	7.0	Tough and difficult to machine in lathe. Long curling chip
		12/16/1913	None	57,200	15,300	24.5	21.9	
		12/22/1913	None	64,100	9,360	25.4	27.0	Fracture coarsely granular and not uniform in appearance
H 15	Co 98.5 Fe 1.0 S 0.020 Ni 0.3 C 0.18 Ca None Si None P None	2/15/1913	None	76,700	33,800	7.7	6.5	
H 87*c*	Co 97.8 Fe 1.46 Si 0.020 Ni 0.5 C 0.18 Ca None S 0.02 P 0.012	1/23/1914	None	56,100	30,600	5.3	5.0	Metal medium hard and tough. Long curling chip. See Fig. VIII
H 87*f*	Co 98.7 Fe 0.80 Si 0.020 Ni 0.2 C 0.22 P None S 0.029 Ca None	4/ 5/1913	None	75,000	33,700	25.4	29.7	Very tough to machine in lathe
H 87*b*	Co 98.5 Fe 0.80 Si 0.020	2/10/1913	None	63,200	33,100	24.1	24.0	
H 87*d*	Ni 0.2 C 0.37 P None S 0.016 Ca None	2/10/1913	None	77,700	33,900	23.8	24.0	
H 211	C 0.18 S 0.08 P 0.031	12/22/1913	None	31,000	31,000	None	None	Segregation of impurities. See Fig. X
"COMMERCIAL COBALT"—Annealed								
H 109	Co 96.8 Fe 2.36 Si None Ni 0.56 C 0.062 P 0.017 S 0.022 Ca None	1/ 9/1914	Annealed from 700° C.	56,100	29,300	13.3	13.0	Metal soft and tough. Machines with medium long curling chip
		1/14/1914	Annealed from 700° C.	52,600	31,600	13.3	13.5	See Fig. IX
H 214*c*	Co 97.09 Fe 1.45 Si 0.011 Ni None C 0.067 P 0.10 Mn 2.04 S 0.012 Ca None	5/19/1914	Annealed at 850° C.	70,500	37,100	5.1	8.0	Very fine grain, uniform. See Fig. V
		5/19/1914	Annealed at 1000° C.	75,200	25,500	6.1	10.0	Very fine grain, uniform. See Fig. VI
H 87*c*	Co 97.8 Fe 1.46 Si 0.020 Ni 0.5 C 0.18 P 0.012 S 0.02 Ca None	4/22/1914	Annealed at 850° C.	60,200	40,800	1.5	1.5	Very fine grain, uniform. See Fig. VII
		5/19/1914	Annealed at 850° C.	55,700	......	....	2.0	
		6/ 2/1914	Annealed at 850° C.	63,800	61,300	0.61	0.5	Very fine grain
		6/ 2/1914	Annealed at 850° C.	58,000	56,100	1.5	0.3	Very fine grain
		6/10/1914	Annealed at 950° C.	57,000	18,000	2.57	2.0	Fracture fine-grained but not uniform in appearance
		6/10/1914	Annealed at 950° C.	58,500	20,400	3.4	2.0	
		6/15/1914	Annealed at 1000° C.	65,000	55,000	3.1	1.9	Fine-grained fracture
		6/15/1914	Annealed at 1000° C.	62,300	40,800	3.1	1.9	
		6/17/1914	Annealed at 1000° C.	42,600	40,800	0.61	0.5	
		6/18/1914	Annealed at 1000° C.	56,000	46,000	1.3	1.0	
PURE COBALT—Unannealed								
H 212	Co 99.9 Fe 0.20 Ni None C None S 0.017	1/ 9/1914	None	29,600	10,200	1.5	2.0	Fracture coarse-grained and crystalline
		1/16/1914	None	35,400	31,400	0.5	4.0	Metal soft and brittle. Short chip
		1/23/1914	None	43,400	43,400	None	None	Fracture coarse-grained and crystalline
		1/23/1914	None	45,800	25,500	1.5	0.5	Fracture coarse with radially crystalline structure
		1/26/1914	None	23,000	23,000	None	None	Fracture coarse with radially crystalline structure. Metal soft and brittle. Short chip
		2/ 3/1914	None	37,900	37,900	None	None	Fracture good with fine grain. See Fig. I
H 213	Co 99.73 Fe 0.14 Ni None C None S 0.019	1/23/1914	None	30,600	30,600	None	None	Fracture coarse-grained, crystalline. Metal soft and brittle. Machines with short chip
		1/23/1914		30,100	30,100	None	None	
		1/23/1914	None	23,000	23,000	None	None	
		2/ 3/1914	None	45,300	23,000	3.0	3.6	Fracture good, fine-grained. See Fig. II
PURE COBALT—Annealed								
H 212	Co 99.9 Fe 0.20 Si None Ni None C None Ca None S 0.017	1/14/1914	Annealed from 700° C.	41,200	41,200	None	None	Fracture coarse-grained, crystalline
		1/27/1914	Annealed from 700° C.	28,100	28,100	None	None	Fracture fairly fine structure. See Fig. I
H 217	Co 99.2 Fe 0.730 Si 0.091 Ni None C 0.036 P 0.0077 Al 0.021 S 0.016 Ca None	6/16/1914	Annealed at 950° C.	34 800	26,600	0.30	0.25	Fracture fine-grained and uniform
		6/17/1914	Annealed at 950° C.	43,600	30,600	1.3	1.0	
WIRES								DIAM.
H 213	Co 99.73 Fe 0.14 Ni None C None S 0.19	1/29/1914	Swaged to wire after special treatment (see pp. 11 & 12)	101,800	......	5.0	8.2	0.117 in.
		2/11/1914		77,000	......	1.0	2.0	0.124 in.
		3/24/1914		90,500	......	8.3	...	0.076 in. Fine-grained fracture

to those for our cobalt tensile strength measurements. The iron used for these measurements analyzed:

Fe..........	99.9 per cent	Mn.......	0.031 per cent
S...........	0.023 per cent	Cu.......	0.028 per cent
P...........	0.004 per cent	Si.........	Trace
C...........	0.010 per cent	Ni and Co	None

The nickel (see Fig. XI) used for the tensile strength tests was the same as that used for the melting point determinations.

A large series of measurements on nickel and iron would be required to fix the values of the tensile strengths with any definiteness; our measurements show them to be approximately as follows:

Cast Nickel—Tensile Breaking Load 18,000 Lbs. per Sq. In.
Cast Iron—Tensile Breaking Load 23,000 Lbs. Per Sq. In.

The rate of cooling of cast metals from the fluid to the solid state is such an important factor in determining the mechanical properties of the metal, that it is just as necessary to know the dimensions of the test bars as it is to know the chemical composition. The above values, for iron, nickel and cobalt, all of which have been made under exactly the same conditions, with a standard "proportional" test bar, are strictly comparable, although they should not be compared with values obtained by other observers on bars of different sizes.

CONCLUSIONS—TENSILE STRENGTH

PURE COBALT. I—The tensile strength of pure cobalt, cast and unannealed, is in the neighborhood of 34,400 lbs. per sq. in. This is the average of 10 measurements on cobalt cast from just above its melting point, allowed to cool in iron mould, and machined in lathe to test bars.

II—The effect on the tensile strength of annealing cast cobalt is to increase its value slightly, although this effect is not marked. The average value of our determinations was 36,980 lbs. per sq. in. for the annealed samples, as compared with 34,400 lbs. per sq. in. for the unannealed samples.

III—The percentage reduction in area and elongation are small for cast pure cobalt as would be expected for the pure metal.

IV—The tensile yield point for pure cobalt is in general very close to the tensile breaking load.

V—The tensile strength of pure cobalt increases very rapidly as the metal is rolled, as is common for most metals. It may easily reach over 100,000 lbs. per sq. in. by being swaged down to a wire.

VI—The tensile breaking load of pure cobalt, cast from just above the melting temperature, allowed to cool in iron mould and turned in lathe to test bar, is greater than either that of iron or nickel prepared and tested under the same conditions.

"COMMERCIAL COBALT." VII—The effect of the addition of carbon is to increase the tensile breaking strength of cobalt very markedly, the value rising from 34,400 lbs. per sq. in. for the pure cast and unannealed metal to in the neighborhood of 61,000 lbs. per sq. in. for cobalt carrying from 0.060 to 0.30 per cent carbon. More exactly, the average of eight measurements, with a carbon content of approximately 0.062 per cent, is 59,700 lbs. per sq. in. Similarly, the average of fifteen measurements, with a carbon content varying in the neighborhood of 0.25 per cent, is 61,900 lbs. per sq. in. However, the average deviation of these individual measurements among themselves is such that no more specific conclusion can be attached thereto. These values refer to cobalt cast from just above the melting point, allowed to cool in iron mould, machined in a lathe, and tested unannealed. The increased tensile strength may not be entirely due to the presence of carbon, for these tests were made on "commercial cobalt."

VIII—The effect of carbon and other impurities in the "commercial cobalt" is to greatly increase the percentage reduction and elongation, which rises in most cases well above 20 per cent.

5—COMPRESSIVE STRENGTH MEASUREMENTS

The measurements of the compressive strength of cobalt were made in the same Riehle universal standard vertical screw power testing machine, of 100,000 lbs. capacity, that was used for the tensile strength measurements.

TEST BARS—All bars for compressive strength measurements were $1^1/_2$ in. long and $^3/_4$ in. in diameter.

There is practically no literature on the compressive strength of cobalt.

We measured the compressive yield point of pure nickel (see Fig. XI) under conditions identical with the above measurements for cobalt and found it to be 20,000 lbs. per sq. in. This was for a sample cast from just above the melting temperature, allowed to cool in iron mould, and tested unannealed.

CONCLUSIONS—COMPRESSIVE STRENGTH

PURE COBALT. I—The compressive strength of pure cobalt, cast and unannealed, is in the neighborhood of 122,000 lbs. per sq. in. This is the average of 5 measurements on cobalt cast from just above its melting point, allowed to cool in iron mould, and machined in lathe to test bars.

II—The effect of annealing on the compressive strength of cast pure cobalt is not very marked; the average of 5 measurements of the compressive strength of annealed cast cobalt is 117,200 lbs. per sq. in. There seems to be a tendency to lower the compressive strength by annealing.

III—The compressive yield point of pure cobalt is 56,100 lbs. per sq. in. for the annealed samples, compared with 42,200 lbs. per sq. in. for the unannealed samples. Thus the yield point seems to be slightly raised by annealing.

IV—The compressive yield point of pure cobalt, cast from just above the melting temperature, allowed to cool in iron mould and machined in lathe to test bar, is considerably greater than that of either pure iron or nickel prepared and tested under the same conditions.

"COMMERCIAL COBALT." V—The effect of the addition of carbon is to increase the compressive breaking strength of cobalt, the value rising well above 175,000 lbs. per sq. in. by the addition of from 0.060 to 0.30 per cent carbon. These values refer to cobalt cast from just above the melting point, allowed to cool in iron mould, machined in lathe, and tested unannealed. The increased compressive strength may not be entirely due to the presence of carbon, for these tests were made on "commercial cobalt."

VI—The effect of carbon and other impurities in the "commercial cobalt" does not seem greatly to affect the yield point through the range of our observation, although on the average from 0.20 to 0.30 per cent of carbon, with the other impurities shown, tends to lower it from 5 to 10 per cent for both annealed and unannealed metal.

VII—The effect of annealing "commercial cobalt" is to lower its compressive strength, our values averaging 140,000 lbs. per sq. in. for the annealed samples, compared with 183,000 lbs. per sq. in. for the unannealed samples.

VIII—The compressive yield point of "commercial cobalt," similarly to that for the pure metal, is slightly raised by annealing; our values average 39,000 lbs. per sq. in. for unannealed samples, compared with 53,000 lbs. per sq. in. for the annealed samples.

TABLE V—COMPRESSIVE STRENGTH MEASUREMENTS OF COBALT

All samples cast from just above melting point, allowed to cool in iron mould and turned in lathe

Sample No.	Analysis	Date	Special treatment	Lbs. per Sq. In. Compressive breaking load	Lbs. per Sq. In. Yield point	Remarks
"Commercial Cobalt"—Unannealed						
H 87*b*	Co 98.5 Fe 0.80 S 0.014 Si 0.020 Ni 0.20 C 0.37 P None Ca None	2/10/1913	None	172,000	29,000	
H 87*c*	Co 97.8 Fe 1.46 S 0.020 Si 0.020 Ni 0.50 C 0.18 P 0.012 Ca None	1/16/1914	None	178,000	52,100	Metal medium hard and tough. Machines with medium long curling chip
H 87*a* and *e*	Co 98.7 Fe 0.80 S 0.030 Si 0.020 Ni 0.20 C 0.23 P Trace Ca None	12/22/1913	None	184,000	47,600	
H 87*d*	Co 98.5 Fe 0.80 S 0.016 Si 0.020 Ni 0.20 C 0.37 P None Ca None	2/10/1913	None	184,000	31,200	
H 109	Co 96.8 Fe 2.36 S 0.022 Ni 0.56 C 0.062 P 0.017	12/22/1913	None	197,500	35,000	
H 211	S 0.080 C 0.17 P 0.031	12/22/1913	None	92,000	41,000	Low value due to segregation of impurities. Fig. X
H 130	Co 96.52 Fe 1.27 S 0.053 Ni 2.00 C 0.305 P 0.015	12/22/1913	None	94,000	36,000	Metal short-grained and brittle. Machines with short chip
"Commercial Cobalt"—Annealed						
H 211	C. 0.17 S 0.080 P 0.031	1/10/1913	Annealed from 700° C.	98,200	54,300	Impurities segregated. See Fig. X
H 214	Co 98.71 Fe 1.45 S 0.012 Si 0.011 Ni None C 0.067 P 0.010 Ca None Mn 2.04	4/21/1914	Annealed at 850° C.	144,000	40,700	Fine-grained and uniform
H 87*c*	Co 97.8 Fe 1.46 S 0.020 Si 0.0 Ni 0.50 C 0.18 P 0.012 Ca None	5/19/1914 6/17/1914	Annealed at 850° C. Annealed at 950° C.	124,000 148,000	56,500 61,000	
Pure Cobalt—Unannealed						
H 212	Co 99.9 Fe 0.20 S 0.017 Si None Ni None C None Ca None	1/10/1913 1/24/1914	None None	88,900 104,800	40,700 40,700	Metal soft and brittle, turned with very short chip
H 213	Co 99.73 Fe 0.14 S 0.019 Ni None C None	1/24/1914	None	154,000	36,200	
H 193*a*	Co 99.6 Fe 0.41 S 0.025 Si None	12/ 9/1913	None	135,800	39,200	
H 193	Ni Trace C None P Trace Ca None	1/10/1913	None	123,900	54,200	
Pure Cobalt—Annealed						
H 212	Co 99.9 Fe 0.20 S 0.017 Si None Ni None C None Ca None	1/16/1914	Annealed from 700° C.	129,100	63,400	
H 213	Co 99.73 Fe 0.14 S 0.19 Ni None C None	1/16/1914	Annealed from 700° C.	114,300	65,600	Metal soft and brittle. Machines with short chip
H 217	Co 99.20 Fe 0.730 S 0.016 Si 0.091 Ni None C 0.036 P 0.0077 Ca None Al 0.021	5/19/1914 5/20/1914 6/17/1914	Annealed at 850° C. Annealed at 850° C. Annealed at 950° C.	102,000 106,000 134,800	45,200 65,600 40,700	

6—MACHINING, ROLLING AND SWAGING OF METALLIC COBALT

TURNING PROPERTIES—Pure metallic cobalt may be readily machined in the lathe, although it is somewhat brittle and yields a short chip. The addition of small amounts of carbon renders cobalt less brittle and the metal then yields a longer curling chip upon turning.

SWAGING OF COBALT—Cast cobalt of extreme purity, which has been cast either in iron or sand moulds, whether cooled slowly or rapidly, cannot be directly swaged down to a fine wire without special mechanical heat treatment.

On the other hand, "commercial cobalt" containing small percentages of carbon as described in this paper, may be readily swaged down from cast bars to wire of any desired diameter.

SWAGING MACHINES—For our experiments on the swaging of cobalt, we used a No. 3 Dayton swaging machine, manufactured by the Excelsior Needle Company of Torrington, Conn.

With this machine the metal is not drawn out, as is the case with wire-drawing machines, but is rather hammered down by being placed within a pair of dies, carried in a slot in the face of a revolving mandrel, outside of which is an annular rack containing a number of hardened steel rollers. The dies thus revolve rapidly around the work which is hammered by them as they pass between opposite pairs of rolls on either side of it.

With this machine it is comparatively easy to swage hard steel into fine wires. The steel will pass through the dies either hot or cold. However, when a bar of pure cobalt, which has been turned in a lathe to give it a smooth uniform surface, was placed in the swaging machine cold, it cracked along its entire length, and broke off at many places. This was repeated several times with different bars of the metal, each time with the same result, showing that the metal could not be swaged cold.

It became evident that pure cobalt must be given some heat treatment before it could be swaged at all. Hence a bar was first annealed from a temperature of 700° C., by heating it slowly to this temperature in a gas muffle furnace, holding it there for a short time, and then allowing it to cool with the furnace, during several hours. It was then heated to different temperatures before being placed in the swaging machine, with the following results:

At 900° C., the metal crumbled in the machine as

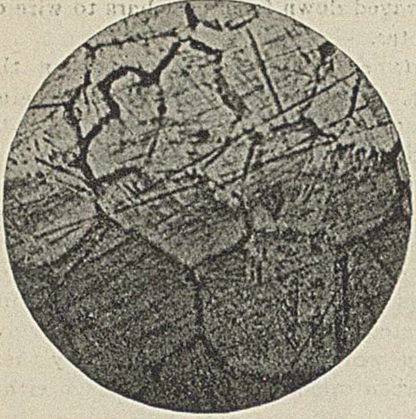

FIG. I × 130 PURE COBALT H 212

Exposure—1 sec.; May 8, 1914
Etching—Strong iodine for 3 minutes
Analysis—Co, 99.9; Fe, 0.20; S, 0.017; Ni, C, Ca, Si, None
Density—8.7562 at 17° C.
Brinell Hardness—128.7
Tensile Breaking Load—37,900 lbs. per sq. in.
Melting Point—1478° C. ±1.1° C.
Specific Electrical Resistance—88.08 × 10^{-7} ohms per cm^3.

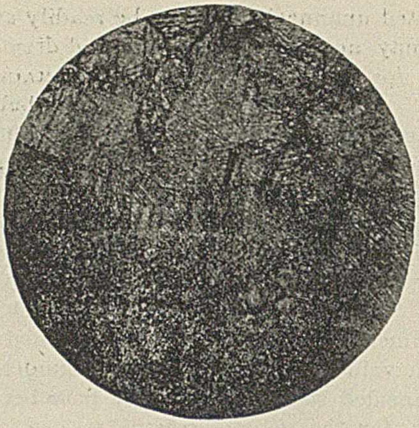

FIG. II × 130 COMMERCIAL COBALT H 213

Exposure—1 sec.; May 9, 1914
Etching—Strong iodine for 5 seconds
Analysis—Co, 99.73; Fe, 0.14; S, 0.019; Si, 0.020; Ni, C, Ca, P, None
Density—8.7732 at 16° C.
Brinell Hardness—121.0
Tensile Breaking Load—45,300 lbs. per sq. in.

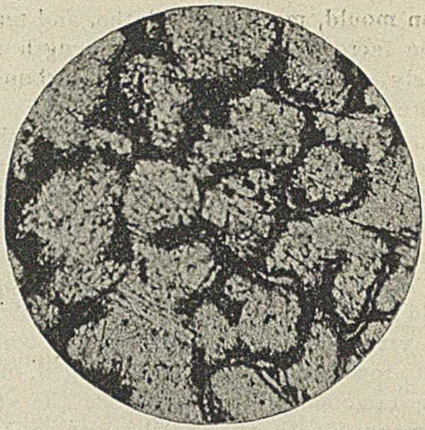

FIG. III × 130 COMMERCIAL COBALT H 214

Exposure—2 sec.; May 1, 1914
Etching—Strong iodine for 14 minutes
Analysis—Co, 98.7; Fe, 1.15; Si, 0.14; S, 0.012; P, 0.011; Ni, Ca, C, None
Density—8.8490 at 15° C.

This sample shows polyhedral crystalline structure, with impurities rejected to the boundaries of the crystalline grains.

though it were extremely hot short, although the sulfur content was as low as 0.018 and 0.020 per cent.

At 700° C. to 800° C. it still cracked and broke very badly in the machine.

At 500° C. to 600° C., however, the bar could be passed through one or two dies without any apparent cracking. It would not go further than this, although the bar was reannealed after each pass, and reductions in diameter of only 0.002 to 0.003 in., on a $^3/_8$ in. bar were made at each pass. At lower temperatures than this the metal would crack still more, and hence it is obvious that the metal must be given some special treatment to render it more ductile before it can be swaged down to a wire.

Cobalt, like iron and certain other metals, will absorb considerable quantities of gases when it is in the molten state; and as the gases in the metal will, in all probability, have a bad effect on its swaging properties, an attempt was made to remove any of these gases that may have been dissolved in the metal and which still remained in the solid bar. With this in view, a bar which had been cast in an iron mould was heated slowly in a good vacuum to a temperature of about 700° C., where it was held for several hours, at the end of which time the bar was allowed to cool slowly in the furnace. This treatment is claimed to have rendered tungsten more ductile; but on attempting to swage a cobalt bar which had been treated thus, very little, if any, improvement was observed in its swaging properties.

The method which finally succeeded consisted in slowly cooling the bar from a high temperature, 1100° to 1150° C., under a high pressure. This was accomplished in the following way: The bar was placed within an iron mould, squeezed tightly by means of clamps, and the whole heated slowly to the above temperature. The mould, with bar, was then removed from the furnace, and the outer portions of the mould chilled while the inner portion still remained hot. The consequent contraction through cooling of the outer portion exerted a considerable pressure on the inner hot bar of metal. The cooling under this pressure continued for three of four hours, after which the metal swaged at a dull red heat with very little difficulty.

The process of swaging consisted in passing the metal, heated to a dull red heat, through successive dies, which hammered it down until a wire of the required diameter was obtained. However, the temperature at which the bar was passed through the dies had to be carefully regulated, as the metal apparently would not swage at all when cold, and when hot only between 500° and 600° C. By thus controlling the temperature, and feeding in the bar very slowly good, smooth, uniform wires were obtained.

CONCLUSIONS—MECHANICAL AND SPECIAL TREATMENTS

I—Pure cobalt may be machined in a lathe as readily as pure nickel or pure iron, although it is somewhat brittle and yields a short chip.

II—"Commercial cobalt," containing small percentages of carbon, machines very readily after the manner of mild steel.

III—Cast cobalt of extreme purity cannot be rolled or swaged without developing cracks, unless given a special mechanical heat treatment.

IV—Cast cobalt of extreme purity may be rolled or swaged to any extent by cooling the casting under extreme pressures, followed by passing through rolls or dies at temperatures between 500 to 600° C., reducing the bar by small percentages at each pass.

V—"Commercial cobalt," containing small percentages of carbon, may be rolled or swaged down from cast bars to any extent, provided that the metal be worked at a red heat.

7—MEASUREMENT OF ELECTRICAL RESISTANCE

The potentiometer method of electrical measurement, which is in reality a measurement of the drop in potential along a known length of wire when a definite current is flowing through it, was employed for our measurements on pure and "commercial" cobalt.

DESCRIPTION OF APPARATUS—Fig. A is a diagrammatic sketch of the electrical circuits as they were used in the potentiometer method of measuring the electrical resistance of cobalt.

W is a storage battery, two volts, which sends a current through the circuit WRDAMCBW, which flows in the direction from R to B. This circuit is known as the potentiometer circuit. AC is a series of fifteen 5 ohm resistance coils, and CB is a 5 ohm slide-wire, consisting of several turns of constantan wire mounted on a marble cylinder. St'd is a cadmium standard cell, electromotive force 1.0189 volts, which bears the certificate of the United States Bureau of Standards. The standard cell is connected from a point X in the coils AC to the switch T, which is set at a point in the resistance DTA, such that the electromotive force between T and X, due to the battery W, is exactly equal to that of the standard cell. This balanced condition is determined by the galvanometer G which is connected in the circuit of the standard cell by throwing the switch U into the dotted position. The resistance R is adjusted until there is no deflection of the galvanometer, which signifies the balanced condition above mentioned.

The resistance coils from A to C are a set of fifteen 5 ohm coils, and the point X is such that ten of them are included between A and X. ATD is a standard resistance such that there is included between A and T exactly 0.945 ohm. When the balance was made, there flowed, therefore, through the potentiometer circuit, a current I = 1.0189/50.945 = 1/50 ampere. This adjustment is made so that for this current in the potentiometer circuit, the drop in potential across any two adjacent coils along AC is exactly 1/10 of a volt.

The switch used is now thrown to connect an unknown electromotive force (E. M. F. in the diagram) through the galvanometer, and in such a way that the current from the new source flows in the same direction as that from the standard cell. The sliding contact M^1 is brought to the zero end of the slide wire, and the moving contact M is shifted from C towards A, step by step, until the galvanometer deflection is reversed in direction. M is left at the last point for which a galvanometer deflection is in the same direction as when M was at C. Then the contact M^1 is moved along the slide wire until the galvanometer deflection is zero.

The reading of the contact point M gives the value of the electromotive force in tenths of a volt, and that of M^1 from hundredths to hundred-thousandths of a volt. Thus a very accurate measurement of the unknown electromotive force is obtained in terms of the known standard.

The unknown electromotive force in these experiments is not a cell, but is the drop in potential along S. S is a given length of the cobalt wire, whose resistance is to be measured, through which a small current is passing from battery W^1 connected as shown in the diagram. In this latter circuit W^1S there is also connected a standard resistance S^1 of 0.1 ohm. By throwing the switch U^1 into the dotted position the drop in potential along S^1 was measured. Knowing the drop in potential along S and also along S^1, when the same current is passing through each, the resistances are known from the following equation:

$$\frac{\text{Unknown Resistance S}}{\text{Known Resistance S}^1} = \frac{\text{Drop in Potential along S}}{\text{Drop in Potential along S}^1}$$

METHOD OF COMPUTATION—The length S between two knife edges, which formed the contact points between which the electromotive force was determined, was carefully measured to tenths of a millimeter. The average diameter of the wire was measured to thousandths of a millimeter, and from these data the specific resistance of the wire in ohms per cubic centimeter was calculated to be

$$R = \mu\frac{l}{A} \text{ or } \mu = \frac{RA}{l},$$

where
R = total resistance of S in ohms,
l = length of S in centimeters,
A = average cross section of S in square centimeters,
U = specific resistance in ohms per centimeter cube.

After this measurement the wire was cut to the exact length S, carefully weighed to the nearest milligram, and the density of the wire determined by the Archimedes principle. From these data the resistance

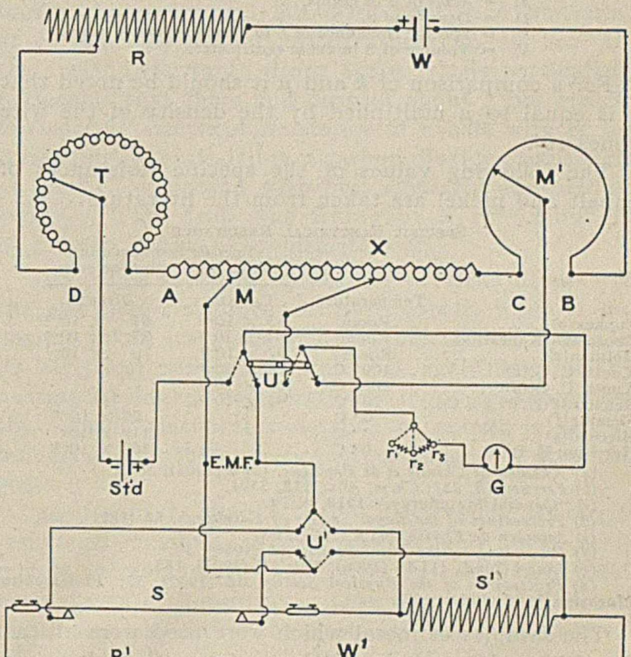

FIG. A—ARRANGEMENT OF CIRCUITS FOR ELECTRICAL RESISTANCE MEASUREMENTS

W and W^1—2 Volt and 4 Volt Storage Batteries, Respectively
R and R^1—Adjustable Rheostats
U and U^1—Double-Throw Switches
G—Galvanometer
R and R^1—Small Resistances for Protection of Galvanometer in Making Adjustments
St'd—Standard Cell, E. M. F. = 1.0189 Volts
S—Wire Tested
S^1—Standard Resistance of 0.1 Ohm Correct to 1/25 of One Per Cent, and with No Temperature Coefficient

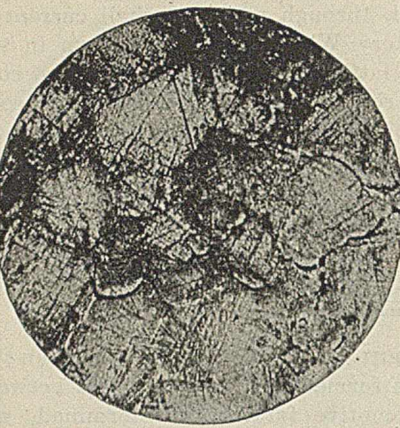

FIG. IV × 130 COMMERCIAL COBALT H 130

Exposure—2 sec.; May 1, 1914

Etching—Strong iodine for 7 min.

Analysis—Co, 96.5; Ni, 2.0; Fe, 1.27; C, 0.305; S, 0.054; P, 0.015

Density—8.7690 at 17° C.

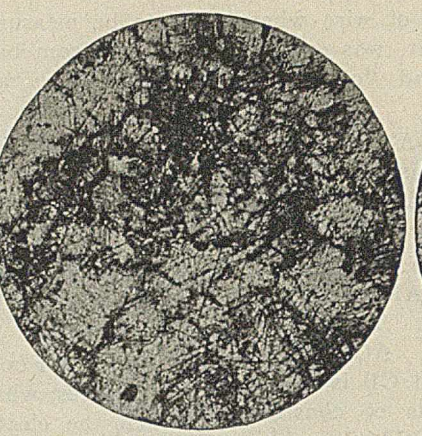

FIG. V × 130 COMMERCIAL COBALT H 214 *c*

Exposure—1 sec.; May 6, 1914
Etching—Strong iodine for 5 min.
Analysis—Co, 97.09; Fe, 1.45; C, 0.067; S, 0.012; Mn, 2.04; Si, 0.011; P, 0.010; Ni, Cu, None
Annealed at 850° C.
Tensile Breaking Load—70,500 lbs. per sq. in.

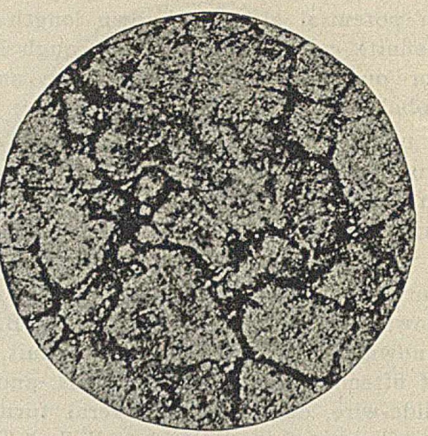

FIG. VI × 130 COMMERCIAL COBALT H 214 *c*

Exposure—2 sec.; May 2, 1914
Etching—Strong iodine for 9 min.
Analysis—Co, 97.09; Fe, 1.45; C, 0.067; S, 0.012; Mn, 2.04; Si, 0.011; P, 0.010; Ni, Ca, None
Annealed at 1000° C.
Tensile Breaking Load—75,200 lbs. per sq. in.

of the wire in ohms per meter gram was calculated as follows:

$$R = \mu\frac{l}{A}.$$

$$D = \frac{M}{V} = \frac{M}{lA}, \quad \text{or} \quad A = \frac{M}{Dl}.$$

from which $$R = D\mu\frac{l^2}{M} = \frac{kl^2}{M}, \quad \text{or} \quad k = \frac{RM}{l^2},$$

where
R = Resistance of S in ohms,
M = Mass of S in grams,
D = Density of S,
k = Specific resistance of S in ohms per meter gram,
V = Volume of S in cubic centimeters.

For a comparison of *k* and μ it should be noted that *k* is equal to μ multiplied by the density of the wire times 10^4.

The following values of the specific resistances of cobalt and nickel are taken from the literature:

SPECIFIC ELECTRICAL RESISTANCE

	Temperature	Specific resistance in ohms per centimeter cube: COBALT	NICKEL
Copaux(*a*)	Room	55×10^{-7}	64×10^{-7}
Reuer and Kaneko(*b*)	Room	64×10^{-7}	77.2×10^{-7}
Hofman(*c*)	Room	97×10^{-7}	70×10^{-7}
Knott, C. G.(*d*)	100° C.	121×10^{-7}	
Knott, C. G.(*d*)	200° C.	159×10^{-7}	
Reichardt (*e*), 99.8% Co.	20° C.	97×10^{-7}	
Fleming(*f*)	0° C.		69×10^{-7}
Niccolai(*g*)	0° C.		119×10^{-7}
Harrison, E. P.(*h*)	0° C.		103×10^{-7}

(*a*) *Annalen de Chimie et de Physique*, [8] **6** (1905), 508.
(*b*) *Ferrum*, **10**, 257; *Chem. Abs.*, **113**, 3591.
(*c*) "General Metallurgy," **1913**, p. 29.
(*d*) *Proceedings of the Royal Society of Edinburgh*, **18** (1891), 303.
(*e*) *Annalen de Physik*, [4] **6** (1901), 832.
(*f*) *Proceedings of the Royal Society*, **66** (1900), 50.
(*g*) *Lincei Rend.*, [1] **16** (1906), 757; [2] (1907), 185.
(*h*) *Proceedings of the Physical Society*, **18** (1902), 57; *Philosophical Magazine*, [6] **3** (1902), 177.

The samples of metal which were used were all cast from just above their melting points, allowed to cool slowly in an iron mould, and thereafter swaged down to wires of given diameters according to the method described under "Swaging of Pure Cobalt." Our results are given in Tables VI and VII.

ANNEALING OF WIRES—The effect of annealing on the conductivity of both pure and "commercial" cobalt was studied. In this connection the annealing was accomplished by two methods.

(1) PASSING A SUITABLE ELECTRIC CURRENT THROUGH THE WIRE IN VACUO—The annealing furnace used consisted of a cylindrical glass tube about 4 ft. long and 2 in. in diameter, and sealed off at the ends with rubber stoppers. Through the ends protruded copper leads and a connection to a vacuum pump. The slack in the cobalt wire, developed upon heating, was taken up by a coiled spring. The approximate temperature was measured by a thermocouple placed against the annealing wire.

TABLE VI—ELECTRICAL RESISTANCE OF UNANNEALED COBALT

Sample No. and analysis	DATE Nov., 1913 and Apr., 1914	WIRE DATA: Temp. ° C.	Length Cm.	Aver. cross section Sq. cm.	Weight Grams	RESISTANCE IN OHMS PER: Centimeter Cube	Meter Gram
"COMMERCIAL COBALT"							
H 192	11/7	21.2	83.25	0.005568	3.9881	229.6×10^{-7}	1.977
Co 99.63	11/7	21.0	50.20	0.005568	2.4051	231.2×10^{-7}	1.992
Ni None	11/7	21.8	50.20	0.005568	2.4051	231.5×10^{-7}	1.993
Fe 0.60							
S 0.023							
C 0.09							
Si Trace							
Ca Trace							
H 193	11/8	21.9	75.07	0.01885	12.3871	144.4×10^{-7}	1.271
Co 92.36	11/8	22.0	51.67	0.01885	8.526	144.5×10^{-7}	1.271
Ni 2.73							
Fe 4.49							
S 0.018							
C None							
H 214	4/3	22.5	74.95	0.006374	4.304	105.8×10^{-7}	0.9530
Co 98.71	4/3	22.5	74.95	0.006374	4.304	105.8×10^{-7}	0.9530
Ni None	4/3	22.0	52.64	0.006419	3.023	105.1×10^{-7}	0.9545
Fe 1.15	4/3	22.0	52.64	0.006319	3.023	104.8×10^{-7}	0.9524
Si 0.14	4/6	16.0	82.56	0.006319	4.723	104.2×10^{-7}	0.9431
Ca None	4/6	15.5	82.56	0.006319	4.723	103.8×10^{-7}	0.9403
S 0.012	4/7	18.0	59.95	0.006305	3.429	104.7×10^{-7}	0.9502
C 0.039	4/7	18.0	59.95	0.006305	3.429	104.7×10^{-7}	0.9502
P 0.010							
PURE COBALT							
H 212	1/22	17	92.81	0.005890	4.863	87.27×10^{-7}	0.7766
Co 99.9	Same	17	92.81	0.005890	4.863	88.04×10^{-7}	0.7834
Ni None	Same	17	50.23	0.005890	2.631	88.08×10^{-7}	0.7838
Fe 0.20	Same	17	50.23	0.005890	2.631	88.22×10^{-7}	0.7840
S 0.017	Same	14	79.41	0.005822	4.113	86.66×10^{-7}	0.7713
C None	Same	14	79.41	0.005822	4.113	86.80×10^{-7}	0.7727
Si None	Same	14	48.98	0.005822	2.538	85.80×10^{-7}	0.7637
Ca None	Same	14	48.98	0.005822	2.538	85.55×10^{-7}	0.7616
H 215	4/2	22	95.38	0.006547	5.432	89.17×10^{-7}	0.7756
Co 99.6	4/4	22	95.38	0.006547	5.432	89.98×10^{-7}	0.7826
Ni None	4/4	23.0	95.38	0.006547	5.432	89.98×10^{-7}	0.7826
Fe 0.191	4/4	23.0	95.38	0.006547	5.432	90.26×10^{-7}	0.7852
S 0.012							
C None							
Si 0.084							
Ca None							
P 0.0066							

(2) HEATING WITHIN AN ELECTRIC FURNACE IN A CO_2 ATMOSPHERE—The furnace used consisted of an iron tube about 4 ft. long and 2 in. in diameter, wound with suitable insulated nichrome wire. The ends, which

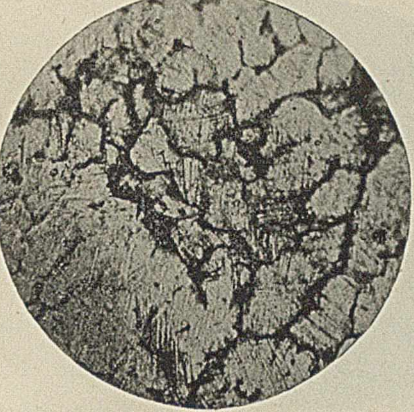

FIG. VII × 130 COMMERCIAL COBALT H 87 *c*

Exposure—1 sec.; May 6, 1914
Etching—Strong iodine for 10 min.
Analysis—Co, 97.8; Ni, 0.50; Fe, 1.46; S, 0.020; C, 0.18; Si, 0.020; Ca, P, Trace.
Annealed at 850° C.
Density—8.6658 at 17° C.
Tensile Breaking Load—60,200 lbs. per sq. in.

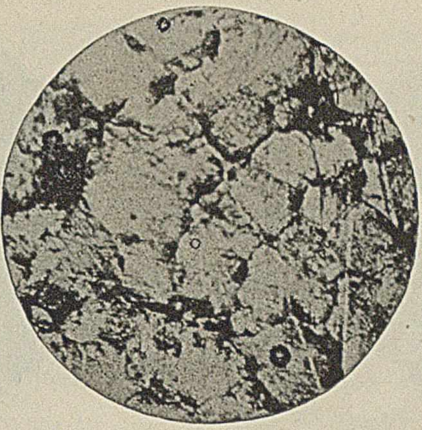

FIG. VIII × 130 COMMERCIAL COBALT H 87 *c*

Exposure—2 sec.; May 5, 1914
Etching—Strong iodine for 1 min.
Analysis—Co, 97.8; Fe, 1.46; Ni, 0.50; C, 0.18; S, 0.020; Si, 0.020; P, 0.012; Ca, None
Tensile Breaking Load—56,100 lbs. per sq. in.

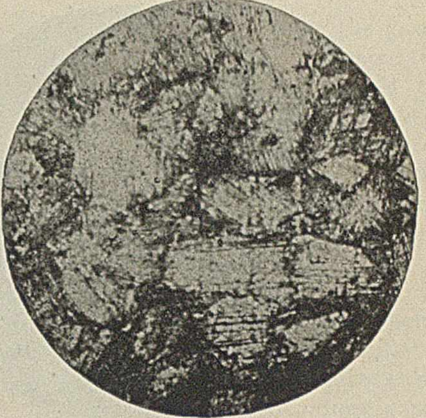

FIG. IX × 130 COMMERCIAL COBALT H 109

Exposure—$^1/_2$ sec.; May 6, 1914
Etching—Strong iodine for 30 sec.
Analysis—Co, 96.8; Ni, 0.56; Fe, 2.36; S, 0.022; C, 0.063; P, 0.017
Density—8.7997 at 18.5° C.
Brinell Hardness—107
Tensile Breaking Load—52,600 lbs. per sq. in.

were sealed off with rubber stoppers, were water cooled and contained a suitable gas inlet and outlet.

CONCLUSIONS—ELECTRICAL RESISTANCE

PURE COBALT. I—The specific electrical resistance of cobalt wires of extreme purity is 89.64×10^{-7} ohms per centimeter cube, or 0.7769 ohms per meter gram, at 18° C. This is the average of twelve observations agreeing well among themselves, and is for wires unannealed after swaging. This is approximately five times that of pure copper.

TABLE VII—ELECTRICAL RESISTANCE OF ANNEALED COBALT

		Wire Data				Resistance in Ohms per		Annealed		
Sample No. and analysis	Date Apr. 1914	Temp. ° C.	Length. Cm.	Av. cross section. Sq. cm.	Wt. Grams	Centimeter Cube	Meter Gram	At ° C.	For hrs.	In
"Commercial Cobalt"										
H 214	11	13.0	74.65	.006333	4.260	91.76×10^{-7}	.8286	350	2	Vac.
Co 98.71	11	13.0	47.50	.006376	2.713	91.49×10^{-7}	.8205	350	5	Vac.
Ni None	21(*a*)	21.5	83.69	.006461	4.845	104.1×10^{-7}	.9325	200	5	CO_2
Fe 1.15	21	21.5	49.97	.006461	2.888	103.7×10^{-7}	.9264	200	5	CO_2
Si 0.14	22	19.2	82.80	.006447	4.799	102.6×10^{-7}	.9225	300	2	CO_2
Ca None	22	19.2	45.86	.006447	2.657	102.9×10^{-7}	.9249	300	2	CO_2
S 0.012	23	19.0	82.40	.006390	.....	100.7×10^{-7}	.9090	400	2	CO_2
C 0.039	23(*a*)	19.0	54.94	.006404	.....	100.2×10^{-7}	.9019	400	2	CO_2
P 0.01	24	18.5	78.11	.006291	4.478	98.42×10^{-7}	.8969	500	2	CO_2
	24	18.5	56.35	.006291	3.230	98.14×10^{-7}	.8941	500	2	CO_2
	25	19.3	81.65	.006319	4.664	93.34×10^{-7}	.8437	600	1	CO_2
	25(*b*)	19.3	57.50	.006319	3.285	93.63×10^{-7}	.8466	600	1	CO_2
	27	15.6	66.67	.006291	3.801	91.44×10^{-7}	.8285	700	1	CO_2
	27	15.8	51.01	.006291	2.907	90.90×10^{-7}	.8232	700	1	CO_2
	28	18.4	53.55	.006263	3.046	90.35×10^{-7}	.8204	800	1	CO_2
Pure Cobalt										
H 215	13	17.7	85.21	.006475	4.834	85.03×10^{-7}	.7449	350	5	Vac.
Co 99.6	13	17.7	85.21	.006475	4.834	85.18×10^{-7}	.7463	350	5	Vac.
Ni None	13	17.7	50.2	.006475	2.848	84.92×10^{-7}	.7424	350	5	Vac.
Fe 0.19	13	17.7	50.2	.006475	2.848	85.04×10^{-7}	.7436	350	5	Vac.
S 0.012	21	19.0	74.44	.006151	4.224	97.42×10^{-7}	.8988	400	2	CO_2
C None	21	18.8	39.89	.006221	2.264	97.94×10^{-7}	.8938	400	2	CO_2
Si 0.084	22	21.2	73.99	.006249	4.162	101.0×10^{-7}	.9108	500	1.5	CO_2
Ca None	22	21.2	49.41	.006249	2.779	101.1×10^{-7}	.9176	500	1.5	CO_2
P 0.0066	23	15.4	72.75	.006249	4.080	93.54×10^{-7}	.8395	600	1	CO_2
	23(*b*)	15.4	52.23	.006221	2.930	93.85×10^{-7}	.8460	600	1	CO_2
	24	19.0	51.37	.006235	2.875	94.06×10^{-7}	.8442	700	1	CO_2
	24	19.0	74.05	.006291	4.145	93.33×10^{-7}	.8360	700	1	CO_2
	28	16.5	73.11	.006207	4.080	91.36×10^{-7}	.8203	800	0.5	CO_2
	28	16.5	54.15	.006207	3.022	91.65×10^{-7}	.8240	800	0.5	CO_2

(*a*) Samples H 214 series, Apr. 21–23, are all the same wire, annealed and unannealed.

(*b*) Note drop in resistance between 500° and 600° C.

II—The effect of annealing cobalt wire of extreme purity *in vacuo*, at about 350° C. for several hours, by passing an electric current through the wire is to diminish its electrical resistance by about 5 per cent. This is not as much as is true of some metals, as for example, aluminum, the resistance of which is diminished about 10 per cent by annealing for 2 hours at 250° C.[1]

III—The effect of annealing cobalt wires of extreme purity in an atmosphere of carbon dioxide gas by heating from an external source is at first to increase the resistance, but with continued annealing at increasingly higher temperatures up to 800° C., the specific resistance drops again. It is particularly noticeable that there is a drop of about 7 per cent in the specific electrical resistance of cobalt wire of extreme purity, annealed in a carbon dioxide atmosphere at 600° C. compared with one similarly annealed at 500° C. This drop was from 101×10^{-7} ohms to 93.5×10^{-7} ohms per centimeter cube.

IV—The fact that annealing *in vacuo* diminishes the electrical resistance of pure cobalt, whereas annealing in an inert gas at low temperatures increases its electrical resistance, which is again lowered by heating at higher temperatures, tends to show that the specific electrical resistance of cobalt is largely influenced by the presence of occluded or absorbed gases.

"COMMERCIAL COBALT." V—The specific electrical resistance of cobalt, as with copper and most other metals, increases tremendously by the addition of small percentages of impurities. Less than 0.5 per cent of impurities may treble the electrical resistance.

VI—The specific electrical resistance of "commercial cobalt" varies between 231×10^{-7} and 103×10^{-7} ohms per centimeter cube, for the cases we have studied, depending upon the nature of the small percentages of impurities present. These figures are for wires unannealed after swaging.

VII—The effect of annealing "commercial cobalt" by passing an electric current through the wire *in vacuo*, is to greatly reduce its specific electrical resistance. Annealing in this way at 350° C. for 5 hours

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[1] H. Gwercke, *Electrician*, **72**, 450; *Chem. Abs.*, **1914**, 1049.

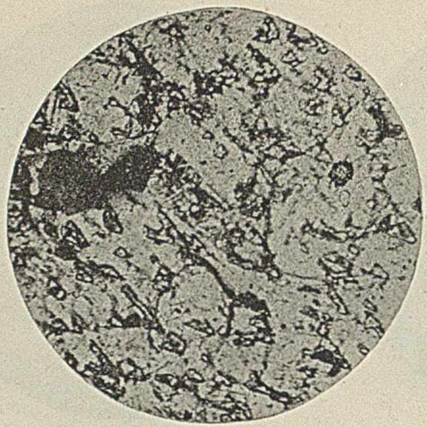

FIG. X × 130 COMMERCIAL COBALT H 211

Exposure—1 sec.; May 5, 1914 Etching—Strong iodine for 1 min.
Brinell Hardness—128.2 Analysis—C, 0.18; S, 0.080; P, 0.031
Tensile Breaking Load—31,000 lbs. per sq. in.

This sample shows "ghosts" or "ghost lines" because of its impurities, C, S, and P. Metals of this kind are usually brittle, weak and hard, which are the characteristics of this particular sample as shown under the tables of measurements preceding.

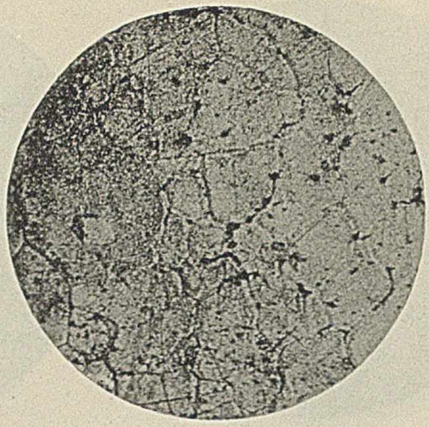

FIG. XI × 130 PURE NICKEL

Exposure—2 sec.; May 7, 1914 Brinell Hardness—83.1
Etching—Nitric acid (sp. gr. 1.42) for 4 sec.
Analysis—Ni, 99.29; Fe, 0.48; S, 0.025; Si, 0.042; Co, Ca, C, None
Tensile Breaking Load—18000 lbs. per sq. in.
Melting Point—1444° C.
This nickel shows polyhedral crystalline structure of the pure metal.

reduced the specific resistance by approximately 14 per cent.

VIII—The effect of annealing "commercial cobalt" in an atmosphere of carbon dioxide gas by heating from an external source is in general to decrease its resistance. As in the case of pure cobalt, there is a sharp decrease in resistance in the sample annealed in an atmosphere of CO_2 gas at 600° C. compared with that similarly annealed at 500° C.

These conclusions all refer to measurements on wires made from bars cast from just above melting temperature, allowed to cool in an iron mould, and then swaged to wires of approximately 0.03 in. diameter, in the manner described on pages 11 and 12.

8—MAGNETIC PERMEABILITY AND HYSTERESIS MEASUREMENTS OF PURE COBALT

A considerable series of measurements on the magnetic properties of pure cobalt have been made in this laboratory, but as they are extended in length, and as they have bearing on certain interesting magnetic cobalt alloys, which are also being studied, these measurements will form part of an independent paper, which is in process of writing.

9—SPECIFIC HEAT MEASUREMENTS

The specific heat of cobalt was determined by the method of mixtures, and the result is probably accurate to within 0.5 per cent.

The method employed consisted in heating a weighed amount of metallic cobalt in the form of short pieces of wire to 100° C., by bringing them into temperature equilibrium with steam at normal temperature and pressure, at the same time having them enclosed so that they were perfectly dry. This was accomplished by a simple boiler device.

When the metal was thus brought to 100° C., which temperature was read on a suitable thermometer, and after constant temperature readings on this thermometer had been obtained for a period of minutes, it was dropped directly from the heater into a suitable calorimeter. Prior to dropping the cobalt at 100° C. into the calorimeter, preliminary temperature readings of the water in the calorimeter were made over a period of minutes. These readings were continued with uniform stirring of the calorimeter liquid, after the introduction of the cobalt, until the final equilibrium calorimeter temperature had been reached.

The thermometer was read to 0.01° C., and readings were taken every 20 seconds. This method obviously gives us the mean specific heat between 100° C. and room temperature, approximately 15° C.

MATERIAL—The cobalt used for the specific heat measurements was Sample No. H 213 (see Fig. II) and analyzed as follows:

Co	99.73	C	None
Ni	None	Si	0.040
Fe	0.14	Ca	None
S	0.019	P	None

The mean of a series of specific heat measurements, made as indicated above, gives us the

Mean Specific Heat of Cobalt between 15–100° C. = 0.1053.

with an average deviation of single observations from the mean of about 0.5 per cent.

The writers wish to acknowledge their indebtedness to Professor W. J. Drisko of the Department of Physics, Massachusetts Institute of Technology, Boston, who was good enough to have several specific heat measurements of our material made under his direction at the Massachusetts Institute of Technology. These measurements were made on the same material as above. Following are the measurements:

SAMPLE H 213, MARCH 18, 1914

	Specific heat of cobalt		Deviation of a single observation from the mean
	0.1070		0.0014
	0.1037		0.0019
	0.1058		0.0002
	0.1060		0.0004
Mean,	0.1056	Average,	0.0010

Mean Specific Heat of Cobalt between 15–100° C. = 0.1056 ∓ 0.0005.

The following values of the specific heat of cobalt are taken from the literature:

Observer	Temperature Range ° C.	Specific Heat	Observer	Temperature Range °C.	Specific Heat
Tilden(*a*)..	—182 to 15	0.0822	Copaux(*c*)..	500	0.1451
	— 78 to 15	0.0939		800	0.1846
	15 to 100	0.1030		1000	0.204
	15 to 185	0.1047	Copaux(*d*)..	20 to 100	0.104
	15 to 350	0.1087	Kalmus and Harper...	15 to 100	0.1053
	15 to 435	0.1147	Drisko......	15 to 100	0.1053
	15 to 550	0.1209			
	15 to 630	0.1234			
Tilden(*b*)..	20 to 200	0.104			

(*a*) *Proceedings of Royal Society*, **66** (1900), 244.
(*b*) *Ibid.*, **71** (1903), 220.
(*c*) *Compt. rend.*, **140** (1905), 657.
(*d*) *Annalen de Chimie et de Physique*, [8] **6** (1905), 508.

From these figures the true specific heat at any temperature may be computed from 0° to 890° C.

Specific Heat = $0.1058 + 0.0000457t + 0.000000066t^2$.

MICROPHOTOGRAPHS

No attempt has been made to make a minute or complete microphotographic study or analysis of cobalt with the small percentages of impurities with which we have to do in this paper. Such a study would be decidedly interesting but, unfortunately, is not possible in the time at our disposal. The microphotographs shown (Figs. I to XI) are rather characteristic, and require no further explanation than the notes accompanying them and the references in the text and tables.

The analyses throughout this paper were made by Mr. R. C. Wilcox, part-time assistant in this laboratory; valuable assistance was rendered in certain of the experiments by Mr. W. L. Savell, B.Sc., and by Mr. K. B. Blake, S.B., likewise both part-time assistants. The authors wish to acknowledge their indebtedness to these gentlemen.

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THE SEPARATION OF THE ILLUMINANTS IN MIXED COAL AND WATER GAS[1]

By G. A. Burrell and I. W. Robertson

In this paper are shown experiments, made by the Bureau of Mines, that resulted in separating the illuminants in the artificial gas of Pittsburgh. This gas is made by mixing 1 part carbureted water gas with three parts of coal gas. The separation was made by fractionally distilling the gas in a vacuum at low temperatures, and follows the method detailed by the Bureau in separating natural gases.[2]

In both the natural gas work and coal gas work, advantage was taken of the work on the subject by P. Le Beau and A. Damiens,[3] who separated mixtures of the paraffin hydrocarbons and coal gas by the same method. The Bureau, however, separated the paraffin hydrocarbons into single constituents and found it necessary to refractionate distillates and residues in all cases to obtain pure gases. Le Beau and Damiens make no mention of this latter necessity and separated the paraffins in pairs. Further, there is shown in this paper a simple method for the determination of benzene in artificial gas. The principle of the procedure rests on the fact that the gases at different stages in the analysis are subjected to temperatures at which certain constituents can be removed by a mercury pump from certain others which have lower vapor tensions at the temperatures selected. It was found impossible to make a clean separation in any case at one fractionation, hence distillates and residues were refractionated until the separation was as complete as was desired.

The following groups show the constituents in artificial gas that can be separated at different temperatures. The first column shows the distillates that can be obtained at a particular temperature and the second column the residues, *i. e.*, those gases that have appreciable vapor pressures at the temperatures given:

Table I—Groups Separated from Artificial Gas at Various Temperatures

Distillates: Name and formula	Distillates: Boiling point ° C.	Residues: Name and formula	B. P. ° C.	Name and formula	B. P. ° C.
Liquid air temperature, —185° C.					
Methane, CH_4...	—165	Ethane, C_2H_6.....	—93	Ethylene, C_2H_4..	—103
Nitrogen, N_2.....	—195	Propane, C_3H_8....	—45	Propylene, C_3H_6	—51
Oxygen, O_2......	—183	*N*-butane(*a*), C_4H_{10}	1	Iso-butylene(*a*), C_4H_8.........	—4
Carbon monoxide, CO...........	—190	Iso-butane, C_4H_{10}	—10	Benzene, C_6H_6...	80
Hydrogen, H_2....	—253				
Below —140° C.					
Ethylene, C_2H_4...	—103	Propane, C_3H_8....	—45	Propylene, C_3H_6	—51
Ethane, C_2H_6....	—93	*N*-butane, C_4H_{10}..	1	Iso-butylene, C_4H_8.........	—4
		Iso-butane, C_4H_{10}	—10	Benzene, C_6H_6..	80
Below —120° C.					
Propane, C_3H_8...	—45	*N*-butane, C_4H_{10}..	1	Iso-butylene, C_4H_8.........	—4
Propylene, C_3H_6..	—51	Iso-butane, C_4H_{10}	—10	Benzene, C_6H_6..	80
—78° C.					
N-butane, C_4H_{10}.	1	Benzene, C_6H_6....	80		
Iso-butane, C_4H_{10}	—10				
Iso-butylene, C_4H_8	—4				

(*a*) The boiling point of *N*-butylene could not be found in the literature. The *N*-butylene was not separated from the iso-butylene; neither was the *N*-butane separated from the iso-butane.

Table II—Composition of the Artificial Gas of Pittsburgh as Analyzed by Ordinary Methods (September 1, 1914)

Constituents	Per cent	Constituents	Per cent
Carbon dioxide, CO_2........	2.64	Methane, CH_4...........	30.96
Oxygen, O_2................	0.81	Ethane, C_2H_6...........	1.82
Illuminants................	8.67	Nitrogen, N_2...........	4.72
Carbon monoxide, CO......	13.34		
Hydrogen, H_2.............	37.04	Total,	100.00

In making the analysis in Table II the carbon dioxide was removed by the caustic potash solution, the oxygen by alkaline pyrogallate solution, the illuminants by fuming sulfuric acid, the hydrogen by absorption in colloidal palladium[1] solution, the methane and ethane by slow combustion, and the nitrogen by difference.

The above gas was next subjected to fractional distillation at various low temperatures in the apparatus shown at Fig. I. At *a* is shown a Dewar flask to hold the refrigerant used in cooling the gases; *b* is the bulb in which the gases were cooled; *d* is a gas-analysis burette and *c* another gas container for measuring the gases prior to cooling; *e* is a pressure gauge for registering pressures in the Töpler pump; *f* is a drying tube containing phosphorus pentoxide for removing the water vapor from the gases; *g*, *h* and *i* are containers for trapping the gases over mercury as they were removed from the pump; *h* and *i* are provided with 3-way stopcocks. The particular advantage of containers such as are shown at *h* and *i*

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[1] Presented at the meeting of the American Gas Institute, October 20, 1914, New York City, with the permission of the Director of the U. S. Bureau of Mines.

[2] Burrell, G. A. and Seibert, F. M., "Gas Analysis by Fractional Distillation at Low Temperatures," *J. Am. Chem. Soc.*, **36** (1914), 1538–1548.

[3] *Compt. rend.*, **156** (1913), 325; **156** (1913), 797.

[1] See Burrell, G. A. and Oberfell, G. G., "The Absorption of Hydrogen by Colloidal Palladium Solution," This Journal, **6** (1914), 992.

lies in the fact that they can be filled with mercury by forcing down on them with the stopcock open to the air, finally filling the capillary tubes with mercury. The gas from the pump can then be introduced into them by means of the goose-neck tube attached to *l*, leaving a mercury seal in the capillary tube all the time; *i* is a pressure gauge which is of principal use in the benzene determination; *o*, *n* and *m* are 3-way stopcocks. A counterpoise, *p*, attached to the mercury reservoir of the Töpler pump greatly facilitates the working of the pump.

Fig. II shows the various steps in the main separation of the gas.

SERIES I—The original volume of sample (2048 cc.) was first freed of the carbon dioxide by passing it through caustic potash solution: 53 cc. of carbon dioxide were removed, leaving 1995 cc. The latter quantity of gas was then cooled in the bulb *b* (Fig. I) (about 300 cc. at a time), at the temperature of liquid air. After the introduction of each 300 cc., pumping was started and as much of the gas removed as possible. There resulted a distillate, A, and a residue, B. The distillate A was fractionated at the temperature of liquid air, resulting in two more fractions, C and D. D was added to the residue B, and the total again fractionated at the temperature of liquid air. The distillate F thus obtained was added to the distillate C, and the total again fractionated at the temperature of liquid air. The residue thus obtained (10 cc.) was added to the residue E, and the total again fractionated. There resulted a distillate, G, of 3 cc. which was added to the distillate I, making a total of 1782 cc. This first series of fractionations shows the general procedure. At the temperature adopted, in this case the temperature of liquid air, the gases were repeatedly fractionated until no more distillate of consequence could be obtained: 3 cc., the final distillate obtained, is only 0.15 per cent of the original quantity of gas (2048 cc.) taken for the experiment. The total distillate obtained at the temperature of liquid air was 1782 cc., and consisted of those gases that have an appreciable vapor tension at that temperature. This fraction, when calculated to the original quantity of gas taken, consisted of 0.81 per cent oxygen, 13.25 per cent carbon monoxide, 37.33 per cent hydrogen, 31.13 per cent methane, and 4.23 per cent of nitrogen. It will be observed that the quantities of these constituents check very well with the quantities of the same constituents found in the ordinary analysis of the coal gas (page 17). The residue H of the first series of fractionations (191.6 cc.) should consist of those gases and vapors that do not have an appreciable vapor pressure at the temperature of liquid air. They are C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, C_4H_8 and C_6H_6; in other words, the so-called illuminants of coal gas with the addition of ethane and probably propane.

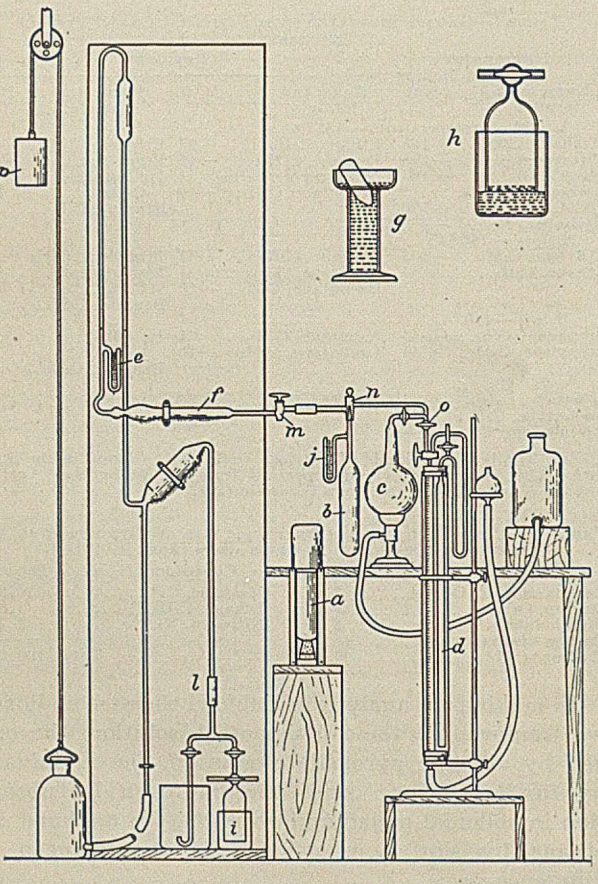

FIG. I—APPARATUS FOR LIQUEFACTION AND FRACTIONATION OF GASES

SERIES II—The residue H (191.6 cc.) was next cooled at a temperature not higher than —140° C. and as much gas removed as possible with the mercury pump. Distillates and residues were repeatedly fractionated until there was obtained 167.0 cc. of gas consisting of ethane and ethylene. The fraction was analyzed in two ways: *first* by burning the entire fraction with oxygen, and *second*, by first removing the ethylene with fuming sulfuric acid and then burning the ethane in oxygen. The data covering these methods are given in Table III:

TABLE III—ANALYSIS OF ETHANE AND ETHYLENE FRACTION

COMBUSTION	Cc.	ABSORPTION AND COMBUSTION	Cc.
Sample taken	15.12	Sample taken	34.18
Oxygen added	94.42	After absorption in $H_2S_2O_7$	8.85
Total volume	109.54	Absorbed by $H_2S_2O_7$	25.33
Volume after burning	78.00	Oxygen added	76.28
Contraction produced	31.54	Total volume for combustion	85.13
Volume after KOH absorption	48.27	Volume after burning	64.95
Carbon dioxide produced	29.73	Contraction	20.18
		Volume after KOH absorption	49.02
		Carbon dioxide produced by burning	15.93
	Per cent		Per cent
Ethane	23.90	Ethane	23.3
Ethylene	74.40	Ethylene	74.1

It will be observed that the ethane and ethylene as found by the two methods of analysis check very well, showing that other gases were not present in the distillate in significant amounts. The percentages as found above were averaged and calculated to percentages of the original quantity of gas taken.

SERIES III—After the removal of the ethane and ethylene, there remained 24.4 cc. of gas which was fractionated at a temperature not higher than —120° C. The distillate, 21.1 cc., was analyzed by burning it in oxygen, and measuring the resulting contraction and carbon dioxide and calculating to propane and propylene. This method does not isolate the gases and hence does not show that other gases than these two were not present. In working on the separation of the paraffin hydrocarbons, however, the Bureau found that propane could be separated from ethane at temperatures between —130° C. and —120° C. Propylene has a boiling point very close to that of propane, and the boiling point of ethylene is not far different from that of ethane; hence it is assumed that propylene and ethylene would respond to the same treatment as the propane and ethane.

SERIES IV — After removing the propylene and propane, there remained a residue of 2.3 cc., only 0.11 per cent of the original quantity of gas (2048.0 cc.). This residue was analyzed by burning it in oxygen, and the contraction and carbon dioxide calculated to butylene. The observed data are given in Table IV.

TABLE IV—ANALYSIS OF BUTYLENE RESIDUE

	Cc.
Volume taken for analysis	2.3
Oxygen added	93.81
Total volume	96.11
Volume after burning	90.53
Contraction produced	5.58
Volume after KOH absorption	82.86
Carbon dioxide produced by burning	7.67

According to the reaction $C_4H_8 + 6O_2 = 4CO_2 + 4H_2O$ there result three volumes contraction and four volumes carbon dioxide, when butylene reacts with oxygen. The contraction and carbon dioxide observed in the above analysis, 5.58 cc. and 7.67 cc., is almost in the ratio of 3 : 4, within the error of making the analysis, hence the data were calculated to butylene. Such a small quantity of gas was available to work upon that there might easily have been a trace of butane present. However, the total quantity compared to the original volume was only 0.11 per cent, or a practically insignificant amount. Benzene that should have appeared in the last fraction did not appear satisfactorily; hence a separate portion of gas was taken for this analysis, as is described later.

The total number of cubic centimeters of gas from the various fractions equals 1782 + 167 + 21.1 + 2.3 = 1972.4 cc. This is exclusive of the benzene. The benzene as found by using a separate portion of the coal gas is 1.33 per cent of the coal gas. Then 2048 cc. × 1.33 per cent = 27.2 cc., and 1972.4 cc. + 27.2 cc. = 1999.6 cc., or within about 4.6 cc. of the amount (1995 cc.) that was fractionated. Considering the number of times the different fractions of gas were handled and measured in the fractionation analysis, this is not a bad check on the operation.

DETERMINATION OF BENZENE

For the benzene determination a separate quantity of gas was used, and advantage taken of an apparatus suggested by Dr. G. A. Hulett, Chief Chemist of this Bureau, for the determination of water vapor in air. Dr. Hulett suggested that air with its moisture be cooled at the temperature of liquid carbon dioxide, that the air be then removed with a mercury pump, and the water vapor be determined, after removing the cooling medium, by measuring its pressure. It was a simple matter to apply this principle to the determination of benzene in coal gas. The procedure was to free the coal gas of water vapor and introduce it into the liquefaction bulb *b* (Fig. I), cool it at a temperature of —78° C. and remove as much gas with the pump as possible. The stopcock *n* on the bulb was then closed and the Dewar flask containing the cooling medium removed. The condensed liquid in the bulb was then vaporized and its pressure read on the manometer *j* (Fig. I). This pressure compared with the original pressure of the gas gave the percentage of benzene in the gas. The results of two determinations are shown in the following table:

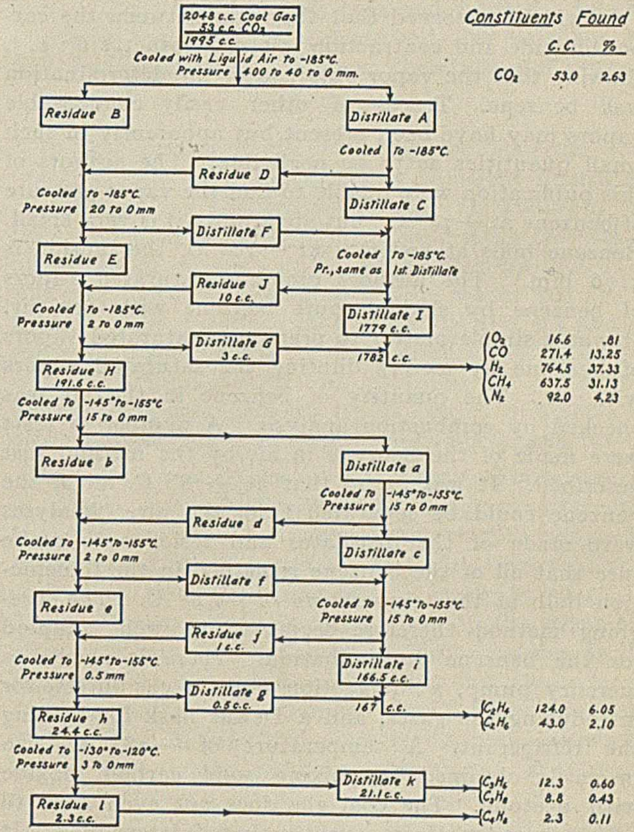

FIG. II—DIAGRAM SHOWING VARIOUS STEPS IN THE FRACTIONATION OF THE COAL GAS OF PITTSBURGH

TABLE V—BENZENE DETERMINATION IN PITTSBURGH GAS

Original pressure of gas, mm. Hg	744	744
Partial pressure of benzene vapor	10	9
Illuminants in distillate—per cent of total gas	7.32	7.39
PER CENT BENZENE	$\frac{10 \times 100}{744} = 1.34$	$\frac{9 \times 100}{744} = 1.31$

The total illuminants in the gas of Pittsburgh as found by absorption in fuming sulfuric acid is 8.67 per cent (page 17). The distillate from the benzene determination was analyzed by absorbing the remaining illuminants in fuming sulfuric acid. There was removed 7.32 and 7.39 per cent of the distillates. These amounts when added to the benzene found, 1.31 and 1.34 per cent, equals 8.66 and 8.70 per cent, or almost identically the same quantities as the total illuminants in the coal gas. Benzene reacts with oxygen as follows:

$$C_6H_6 + 7.5O_2 = 6CO_2 + 3H_2O$$

The contraction is 2.5 volumes and the carbon dioxide is 6 volumes. The following data show the results of analysis of the residual vapor that was held in the liquefaction bulb (Fig. I) when the coal gas was cooled at a temperature of —78° C. Before analysis the benzene vapor was diluted with air.

TABLE VI—ANALYSIS OF BENZENE VAPOR

	Cc.
Volume taken for analysis	28.29
Oxygen added	51.94
Total volume	80.23
Volume after burning	75.47
Contraction due to burning	4.76
Volume after KOH absorption	64.25
Carbon dioxide produced by burning	11.42

It will be observed that the ratio between the carbon dioxide and contraction is almost exactly 6 : 2.5, showing that the vapor obtained in the determination was benzene. Traces of other easily condensable vapors may have been present but apparently in such small quantities as to be negligible. The authors of this publication were unable to find the vapor pressure of benzene at —78° C., but apparently it is very small. Benzene boils at 80° C. At —20° C. the tension is 5.76 mm.[1] The authors prepared saturated vapors of benzene by shaking pure benzene with dry air. It was a simple matter to prepare unsaturated vapors of benzene by merely diluting the saturated vapors with air. The quantity of benzene in the air was checked by combustion analysis. A number of tests were made of the benzene in air by the method just described. It was found that at —78° C. all of the benzene could be separated from the air. Analyses were made of the distillates and residues to make sure that all of the benzene remained in the liquefaction bulb at the temperature of —78° C. The foregoing method therefore seems to be well adapted for the benzene determination. There is needed a mercury pump, a liquefaction bulb, a gas burette for introducing the gases, and a Dewar flask for holding the refrigerant. A temperature of —78° C. can be easily obtained by mixing solid carbon dioxide with acetone. The coal gas does not even have to be measured and its exact volume determined. It is sufficient to introduce it into the liquefaction bulb at atmospheric pressure and then to read the barometer.

The complete analysis of the artificial gas as found by the foregoing methods is given in Table VII.

TABLE VII—COMPLETE ANALYSIS OF ARTIFICIAL GAS OF PITTSBURGH

Constituent	Per cent	Constituent	Per cent
Carbon dioxide, CO_2	2.63	Ethylene, C_2H_4	6.05
Oxygen, O_2	0.81	Propylene, C_3H_6	0.60
Carbon monoxide, CO	13.25	Butylene, C_4H_8	0.11
Hydrogen, H_2	37.33	Benzene, C_6H_6	1.33
Methane, CH_4	31.13	Nitrogen, N_2	4.23
Ethane, C_2H_6	2.10		
Propane, C_3H_8	0.43	TOTAL	100.00

ANALYSIS OF A DIFFERENT SAMPLE OF ARTIFICIAL GAS

Table VIII gives the analysis of a sample of the artificial gas of Pittsburgh collected at a different date than the one already given. It is interesting as showing the marked uniformity of the gas as collected on two days about seven weeks apart. The benzene was not determined in this analysis because the method had not been perfected.

TABLE VIII—ANALYSIS OF A SAMPLE OF ARTIFICIAL GAS OF PITTSBURGH MADE ON JULY 10, 1914

Constituent	Per cent	Constituent	Per cent
Carbon dioxide, CO_2	2.40	Ethane, C_2H_6	1.92
Oxygen, O_2	0.61	Propane, C_3H_8	0.32
Carbon monoxide, CO	13.63	Ethylene, C_2H_4	6.36
Hydrogen, H_2	37.13	Propylene, C_3H_6	0.70
Methane, CH_4	30.92	Butylene, C_4H_8	0.12

HEATING VALUE OF THE ILLUMINANTS IN THE GAS OF PITTSBURGH

In calculating the heating value of artificial gas from the analysis as ordinarily made, a value is usually assigned to the illuminants that is an approximation because the constituents that make up the illuminants have not been exactly known. With these data at hand for the gas of Pittsburgh the authors show below a value calculated from the complete analysis:

TABLE IX—HEATING VALUE OF THE ILLUMINANTS IN ARTIFICIAL GAS

Constituents	B. t. u. per cu. ft. at 0° C. and 760 mm.(a)	Per cent present in the gas	Heating value of constituents present in the gas
Ethylene	1673	6.05	101.21
Propylene	2509	0.60	15.05
Butylene	3265	0.11	3.59
Benzene	4012	1.33	53.36
Propane	2654	0.35	9.29
Total		8.44	182.50

(a) These heating values were calculated from the values as found by Thomsen. His values are given in Landolt and Börnstein's "Physikalish-Chemische Tabellen," 1905, p. 425. They are given in large calories per gram-molecule.

According to the above calculations the illuminants have a heating value at 0° C. and 760 mm. of pressure of $\frac{182.50 \times 100}{8.44} = 2162$ B. t. u. The authors have included propane in the illuminants as ordinarily determined by absorption in fuming sulfuric acid because propane dissolves to a certain extent in the acid. Just how much is not known. It was found that the methane and ethane[1] were soluble to a slight extent. Unquestionably propane is much more so because the higher paraffins are more soluble than the lower ones. Excluding propane, the heating value of the illuminants becomes $\frac{173.2 \times 100}{8.09} = 2141$ B. t. u. per cubic foot at 0° C. and 760 mm. pressure.

ADDITIONAL DETAILS OF THE EXPERIMENT

Temperatures higher than the temperature of liquid air were obtained by cooling a natural gas condensate. This condensate was obtained from a natural gas gasoline plant by subjecting natural gas (casing-head gas) from an oil well to a pressure of 250 pounds per square inch and then cooling it to ordinary temperatures. A steel cylinder, such as is used in transporting oxygen, was shipped to the natural-gas gasoline plant of the Bessemer Gas Engine Company at Follansbee, West Virginia, for the purpose of collecting the condensate. This condensate is known in the natural-gas gasoline trade as "wild" gasoline. It contains large quantities of liquid propane and the butanes, especially the latter, as well as some of the ordinary gasoline constituents, the pentanes, hexanes, etc. Ordinary refinery gasoline, and other substances such as alcohol, ether, methyl and ethyl chloride, jellied so much at low temperatures that they could not be used satisfactorily. In order to obtain a tem-

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[1] Landolt and Börnstein, "Physikalish-Chemische Tabellen," 1905, p. 143 (according to Regnault).

[2] See Burrell, G. A. and Seibert, F. M., "The Sampling and Examination of Mine and Natural Gases," U. S. Bureau of Mines, *Bull.* 42, 47.

perature higher than the temperature of liquid air, say —140° C., the condensate was placed in a Dewar flask and stirred with a test tube into which liquid air was run until —140° C. was reached. Upon removal of the test tube containing the liquid air the condensate warmed up slowly, about 5° C. to 10° C. per hour, thereby affording sufficient time for the withdrawal of the vapors. If the condensate rose to a higher temperature than was desired it was a simple matter to introduce a little more liquid air and cool it.

Temperature measurements were made with two pentane thermometers. They agreed with each other and gave within 1.5° C. the true melting points of chloroform and carbon disulfide, and the temperature of solid carbon dioxide and acetone. Fresh liquid air as it usually reached the laboratory from a plant near-by had a temperature of —193° C.

The determinations of the traces of hydrogen sulfide, acetylene, carbon disulfide, ammonia, etc., that might have been present in the gas were not attempted.

Future work on the fractionation of artificial illuminating gas will cover the analyses of gas that is used in other cities than Pittsburgh and the separation of the illuminants in the coal gas before it is mixed with carbureted water gas and in oil gas that is used to enrich water gas.

Chemical Laboratory
U. S. Bureau of Mines
Pittsburgh, Pa.

SPECIFIC GRAVITY—ITS DETERMINATION FOR TARS, OILS AND PITCHES

By John Morris Weiss

Received September 24, 1914

To the average chemist, the subject of specific gravity is one which, on first glance, seems to present few, if any, difficulties. It is a property which is an absolute quantity for any substance at a given temperature. Unlike many of the other properties of substances determined in the tar industry, it is not an arbitrary figure obtained by a very definite method with very careful attention to manipulative details, but may be determined by any method which is theoretically correct, that is, when the mass and volume relative to water are determined at any specified temperature. Therefore, it would seem that on this test, at least, laboratory workers should have no difficulty in obtaining consistent check determinations, both with themselves and others.

As a matter of fact, it has been the writer's experience, so far as tar products are concerned, that very few tests are susceptible of as grave differences in individual results as the specific gravity test. In the writer's opinion, this is due partly to the fact that all workers do not give sufficient attention to the importance of detail in this test, so that often a method, perfectly correct theoretically, may, by unintentional neglect, give incorrect results when carried out in practice. It is therefore necessary to select a method based on sound theory, which can be carried out with the minimum amount of care by the worker, and then so standardize the details of manipulation that, if directions are followed, the true result will be obtained with a sufficient accuracy for the purposes involved.

It is the writer's intention to review the specific gravity methods now in standard use in the laboratories of the Barrett Manufacturing Company, in the hope that they may be of use to chemists who have to carry out specific gravity determinations on tar and tar products, or other similar materials. Most of the *special methods* described have been developed to a large extent in the writer's own laboratory. The descriptive part of this paper may be divided into two parts: *First*, oils; *Second*, tars and pitches. In the course of the paper, attention will also be given to temperature correction factors, their use and misuse.

I—OILS

In this connection we shall consider oils from coal tar and other tars; presupposing sufficient quantities of material for the ordinary test. In addition, we shall deal with methods that are used when only small quantities of oil are available (less than 20 cc.) as is the case in road compound testing, where the specification calls for the distillation of 100 g. and a subsequent specific gravity of the distillate oil; and also, when a Hempel distillation, according to the Forest Service method for creosote oils, is carried out, and specific gravities are required on the narrow fractions taken.

A. OVER 100 CC. OF OIL AVAILABLE—For any ordinary work, a standardized hydrometer gives sufficiently accurate results. Our custom for creosote oils is to have a set of three, *i. e.*, 1.000 to 1.080, 1.070 to 1.150, and 1.150 to 1.230, compared to water at 15.5° C. These are approximately 225 mm. long; the stems are about 125 mm. in length and the bulbs 24 mm. in diameter: such dimensions adapt them for use in a 100 cc. cylinder of the ordinary type. They are subdivided to 1 in the third place of decimals. For oils lighter than water, similar hydrometers of different ranges are used.

The standard temperatures at which the specific gravities of creosote oils are taken are 15.5° C./15.5° C., and 38° C./15.5° C. As most oils are liquid at 38° C., there is no reason why specific gravities should not, when that temperature is required, be taken at that exact point. If, however, for any reason the reading is taken at a point above the one desired, as is often the case, a correction may be made by adding 0.0008 for every degree Centigrade the temperature is above the standard. To express this in a formula:

$$\text{Sp. gr. } 15.5^\circ/15.5^\circ = \text{Sp. gr. } X^\circ/15.5^\circ + 0.0008\,(X^\circ - 15.5^\circ)$$

If, for any reason, a specific gravity bottle or pycnometer is used at a temperature higher than normal, this correction cannot be applied directly. It is clear that with a pycnometer, the oil must be compared with water at the same temperature, owing to the fact that the absolute capacity of any container varies with the temperature. It is necessary first to calculate the specific gravity X/15.5° from the found figure of X/X and then apply the correction factor given above. This can be done conveniently by multiplying the figure at X/X by the specific gravity of water at X° compared to water at 15.5°. The figure for water can be obtained or calculated from density tables given in many reference books. That is:

$$\text{Sp. gr. } 15.5°/15.5° = \text{Sp. gr. } X/X \times \text{Sp. gr. water } X/15.5° + 0.0008\ (X - 15.5°)$$

It should be borne in mind that this correction factor of 0.0008 per degree centigrade is to be used only on coal tar creosote oils. It is necessary because these oils are frequently solid at 15.5° C., and the specific gravity must of necessity be taken at a higher temperature. Coal tar light oils and distillates from other tars are usually liquid, and can be taken at 15.5° C. Therefore, no very exact correction figure for such substances has been determined. However, if great accuracy is not desired, the same factor can be used for these other materials, if suitable means of cooling are not at hand.

B. LESS THAN 100 CC. BUT NOT MORE THAN 20 CC. OF OIL AVAILABLE—Such cases are comparatively rare, the occasions being when a two-ounce mailing sample is received by a laboratory, and, therefore, there is insufficient for a hydrometer test. Here it is best to use a Westphal balance with the regular plummet. It is necessary in this case to take the specific gravity compared to water at the same temperature, and correct to the desired temperature in the same way as described under A, for the correction of pycnometer gravities.

C. LESS THAN 20 CC. OF OIL AVAILABLE—The method described can be used when as little as 8 cc. of oil are available, and is rapid, convenient, and sufficiently accurate. Any laboratory possessing a Westphal balance can readily use it. As its largest use is in taking specific gravities of small fractions obtained from a Hempel distillation of creosote oil, and as these frequently have limpid points above 50° C., we have fixed on 60° C. as the standard temperature at which to make such measurements. A special plummet is used, which is small enough to go in an ordinary 10 cc. cylinder. This plummet can be made readily by any laboratory worker with elementary glass-handling knowledge.

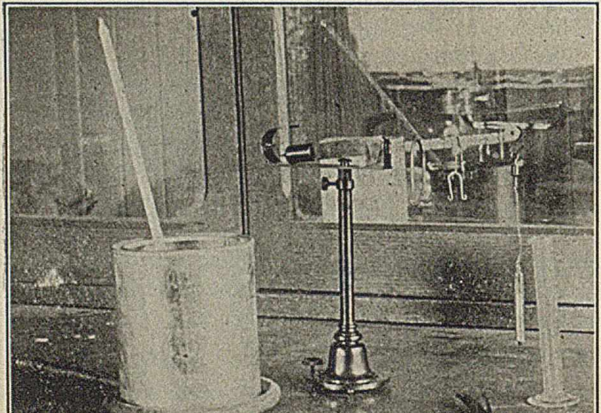


FIG. I

A piece of ordinary glass tubing of about 7 mm. outside diameter is sealed at one end with a short platinum wire melted into the glass where sealed. This is allowed to cool, and about 9–10 g. of mercury, making a column about 35–40 mm. high, is placed in the tube. It is now cut off to within 20 mm. of the top of the mercury, and sealed off with a blowpipe flame. The plummet when completed is about 55–60 mm. long over-all, and should have a weight of from 10 to 12 g. A picture of the Westphal balance equipped with such a plummet, is shown in Fig. I. Beside the balance is shown the heating bath used, which consists of a quart open-top tin can and a ring burner.

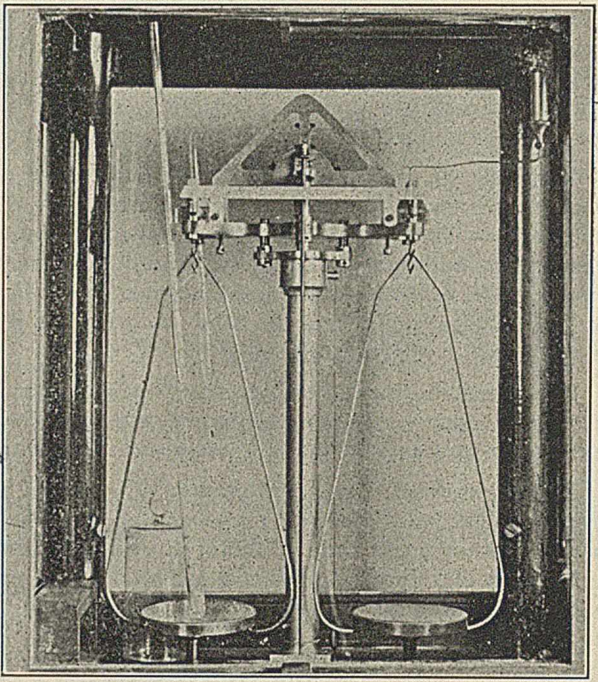


FIG. II

In using the plummet, the weight necessary to balance it in both air and water at 60° C. is noted. Similarly, the weight required to balance the plummet in oil at 60° C. is observed. Then

If a = weight required to balance plummet in air,
b = weight required to balance plummet in water,
c = weight required to balance plummet in oil,

$$\text{Specific Gravity of Oil} = \frac{c - a}{b - a}.$$

That this is theoretically correct may be shown by the following reasoning: $b - a$ represents the lifting force exerted by water on the plummet, or, a volume of water equal to that of the plummet has a weight which is represented by $b - a$. Similarly, $c - a$ represents the weight of a volume of oil equal to the volume of water whose weight is represented by $b - a$. As with equal volumes, specific gravity is taken as the relative weight of the substance to water,

$$\text{Specific Gravity of Oil} = \frac{c - a}{b - a}, \text{ as given above.}$$

Occasionally, especially in road compound specifications, the specific gravity of the oil at 15.5°/15.5° is required. This may be obtained approximately by multiplying the figure found at 60°/60° by the specific gravity of water at 60°/15.5°, and adding 0.036 to the result.

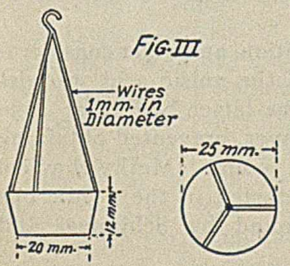
Sometimes there is even too little of the fraction for this method, in which case recourse must be had to some other device. A 1 cc. specific gravity bottle may be used, but we have found that a 1 cc. pipette and a piece of sealed glass tubing, as shown in Fig. II, is very convenient for this purpose. The pipette is standardized by drawing water at 60° C. up into the pipette several times to warm it, then adjusting to the mark, wiping off the outside with a bit of soft paper, inserting it in the glass tube sealed at one end, and weighing it on the balance. The pipette is then dried and the process repeated with the oil to be tested. A piece of rubber tubing on the end of the pipette, which is removed before weighing, serves to protect it from the moisture of the mouth. A small piece of German silver wire, twisted about the pipette near the top, is formed into a ring to support it from the hook above the balance pan (see Fig. II). With this arrangement, results accurate only in the second place of decimals can be obtained.

II—TARS AND PITCHES

A. TARS—With tars, the method used depends on the consistency of the materials handled. For thin materials, like water gas tars, a specific gravity bottle which is a combination of the Regnault and the Hubbard types, of approximately 50 cc. capacity, is usually employed, filling the bottle with tar and adjusting to the mark at the specified temperature of 15.5° C. The water content of the bottle having been predetermined at the same temperature, a simple division gives the specific gravity.

For the more viscous coal tars, such a method is not applicable. Our standard practice on these materials is to use the same type specific gravity bottle[1] and partially fill with tar, adjusting to the mark with water. This method, however, has several disadvantages, *i. e.*, it is slow and tedious, the large-mouth bottle has a tendency to leak if the stopper is not very carefully ground, and there is considerable breakage of the bottles.

Accordingly, we developed in our laboratory what we call the "platinum pan method," and use it almost exclusively for viscous tars and pitches. A drawing of this pan is shown in Fig. III, and a picture of the same in use in Fig. IV. It is made entirely of platinum, and the supporting wires are joined to the pan and to each other by heavy platinum solder. It has a total weight of about 7 g. The method of use is simple. It is suspended from the balance pan by a fine, waxed silk thread, and its weight in air and water at 15.5° C. determined. The pan is then ignited over a burner, let cool, and filled with tar. The weight of the pan filled with tar is taken first in air and then in water at 15.5° C.


Fig·III

Let a = weight of pan in air.
b = weight of pan in water.
c = weight of pan plus tar in air.
d = weight of pan plus tar in water.

$$\text{Then Specific Gravity of Tar} = \frac{c - a}{(b + c) - (a + d)}$$

After the test, the pan is held by a pair of tongs and warmed over a burner, the tar poured out, the pan dipped in benzol or naphtha, and burned off, the entire cleaning operation being complete in two minutes. One standardization suffices for a considerable period of time, and need be repeated only when a new thread is taken, or when high-ash materials, such as blast furnace tar, are being handled. The method is quick, clean and accurate.

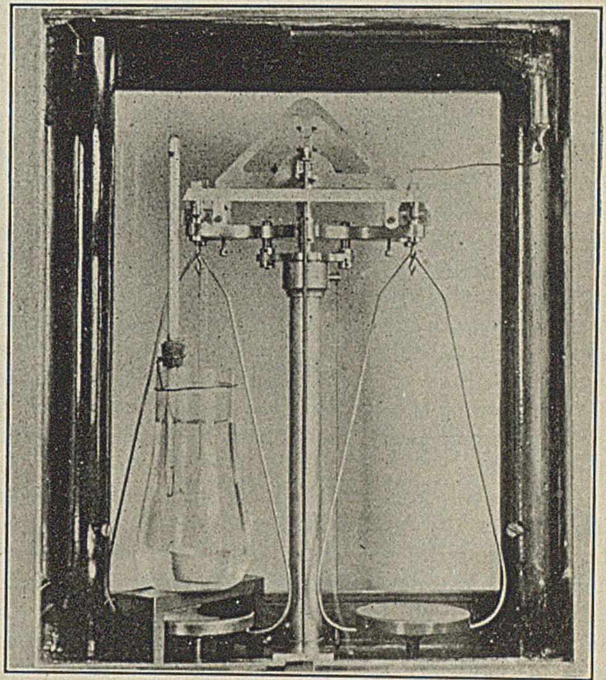


Fig. IV

The use of the hydrometer on tars, though close enough for very rough work, is not to be recommended. For coal tar works tests, it is sometimes used, a factor of 0.000685 per degree centigrade being used as a temperature correction.

B. PITCHES—Here the bottle method is standard for the softer pitches, with the alternative of suspension by a thread in air and water for pitches which are hard enough. For the same general reasons given under tars, we find the pan method more convenient and equally accurate. A lump of the pitch, if hard enough, is used without melting. In the harder pitches, good checks are not obtained as readily as with softer ones. This is because in cooling the melted material, voids are formed in the interior, due to contraction after the surface has hardened. For ordinary work, our practice is to take a lump of the pitch as it comes to hand, though in some very exact work we have slowly

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[1] S. R. Church, THIS JOURNAL, 3 (1911), 227; 5 (1913), 195.

cooled the pitch under slight pressure, to avoid the formation of voids. The slow cooling always caused a marked increase in apparent specific gravity with the harder pitches, while with soft pitches the difference is negligible.

The writer hopes that this paper on the homely subject of specific gravity will be useful in some measure to workers in general, and can state that, in his experience, the methods recommended here are rapid, convenient, and sufficiently accurate.

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OILS OF THE CONIFERAE: IV. THE LEAF AND TWIG OILS OF DIGGER PINE, LODGEPOLE PINE, AND RED FIR

By A. W. SCHORGER

Received November 2, 1914

It is well known at the present time that the oleoresins of the digger pine (*Pinus sabiniana*) and Jeffrey pine (*Pinus jeffreyi*) yield oils consisting almost entirely of *n*-heptane. Examination of the leaf and twig oil of the digger pine has revealed the very interesting fact that heptane was present in the sample to the extent of only about 3 per cent, the remainder of the oil consisting of aromatic bodies which are principally terpenes. It may be assumed with safety that this small percentage of heptane was derived from the small twigs during distillation, since the latter were not separated from the leaves. The phytochemical processes taking place in the leaves and in the woody portions of the tree are, accordingly, entirely different, since the oil from the former consists of aromatic compounds and the oil from the latter of aliphatic derivatives.

Anisic acid was obtained by oxidation of certain fractions of the oils from digger and lodgepole pines. Lack of material prevented obtaining conclusive evidence as to the parent substance from which the anisic acid was derived, and for the same reason the presence of borneol and certain terpenes can not be shown with absolute certainty. The data obtained, however, should be of important assistance to the chemist who is fortunate enough to obtain material for further investigation.

LEAF AND TWIG OIL OF DIGGER PINE
(*Pinus sabiniana*, DOUGL.)

The physical and chemical constants of the oils are given in Table I.

The sample of 238 grams gave the following fractions: 100°–152°, 6.0 per cent; 152°–160°, 10.0 per cent; 160°–170°, 52.0 per cent; 170°–188°, 15.0 per cent; 188°–235°, 8.5 per cent; 235°–290°, 2.3 per cent; residue, 6.0 per cent.

HEPTANE—The lower boiling portions of the oil were fractionally distilled and repeatedly treated with concentrated sulfuric acid. By this treatment 7.2 grams (3.0 per cent) of oil were finally obtained, having the specific gravity 0.7013 at 15° and boiling between 98.5° and 101°. Pure *n*-heptane boils at 98.4° and has a specific gravity at 15° of 0.6880.

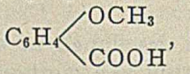
α-PINENE—The fraction boiling at 156–157° had $d_{15°}$ 0.8618 and $\alpha_{D20°}$ —26.24°. A good yield of pinene nitrosochloride was obtained. The nitrosochloride was thoroughly washed with methyl alcohol and dissolved in a small amount of hot chloroform. The crop of crystals obtained on cooling, after washing with alcohol, melted at 104–105°. From the chloroform mother liquor a further amount of crystals was obtained on addition of methyl alcohol. These crystals after washing with methyl alcohol melted at 105°. The nitrolpiperidine derivative melted at 117°. The total α-pinene fractions amounted to 58 to 59 per cent.

TABLE I—THE PHYSICAL AND CHEMICAL CONSTANTS OF THE LEAF AND TWIG OILS

Sample	Sp. gr. 15°	Ref. Ind. 15°	Optical rotation $\alpha_{D20°}$	Acid No.	Ester No.	Ester No. after acetylation	Per cent yield of oil
DIGGER PINE:							
2493	0.8566	1.4670	—20.93°	2.05	11.98	37.16	0.102
2494	0.8543	1.4708	—38.36°	1.91	9.48	29.84	0.085
2496	0.8517	1.4671	—30.75°	1.47	6.77	25.86	0.078
LODGEPOLE PINE:							
2495	0.8690	1.4831	—17.84°	0.90	6.02	32.30	0.234
RED FIR:							
2529	0.8665	1.4861	—16.70°	0.75	9.93	36.22	0.154

The relatively small amount of oil boiling between 160–170° was examined for β-pinene with negative results.

LIMONENE—The total limonene fractions amounted to about 24 per cent. The fraction boiling at 170–175° and having $\alpha_{D21°}$ —40.79° gave negative results for phellandrene. Sylvestrene was apparently absent since the dihydrochloride obtained melted at 49–50°. The fraction boiling at 175–177° yielded a tetrabromide melting at 104°, the melting point of limonene tetrabromide.

ESTER FRACTION—The portion boiling at 206–235° was saponified and distilled with steam. The recovered oil was then oxidized with a saturated solution of potassium permanganate and again distilled with steam. Only a few drops of oil having the odor of camphor were obtained. On acidifying the oxidation liquor an acid was obtained that crystallized from hot water in thin needles and sublimed readily, giving crystals melting at 183–184°. A portion of the acid weighing 0.1637 g. required 10.62 cc. of *N*/10 NaOH for neutralization, giving a neutralization equivalent of 154.2. The properties of the acid showed it to be anisic acid,  $C_6H_4\begin{cases}OCH_3\\COOH\end{cases}$, the latter melting at 183–184° and having a neutralization equivalent of 152.

The boiling point of the fraction, and other considerations, render it probable that the anisic acid was derived from methylchavicol, the latter boiling at 215–216°. Lack of material, however, prevented obtaining conclusive evidence on this point. Methylchavicol has never been previously detected in the needle oils of the coniferae but was found by Schimmel and Company[1] in "pine oil."

"GREEN OIL"—Only a few drops of oil distilled between 235 and 265°. Between 265 and 290°, 5.4 grams (2.3 per cent) of a light green oil were obtained. When a drop of the oil was dissolved in glacial acetic acid

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[1] Report for April, 1910.

and a drop of concentrated sulfuric acid was added the solution turned saffron, then crimson.

LEAF AND TWIG OIL OF LODGEPOLE PINE
(*Pinus contorta*, LOUD.)

The physical and chemical constants of the lodgepole pine oil are given in Table I.

The sample examined amounted to 414 g. and gave the following results on distillation: 164°–170°, 40 per cent; 170–175°, 27 per cent; 175–183, 10.5 per cent; 183–205°, 5.5 per cent; 205–235°, 7 per cent; 235–255°, 0.5 per cent; 255–284°, 6.5 per cent.

FURFURAL—A qualitative test for furfural was obtained in the aqueous extract of the first fraction by means of aniline and hydrochloric acid.

α-PINENE—After repeated fractionation, 12.6 g. (3 per cent) of oil were obtained, having the following properties: b. p. 156–160°, $d_{15°}$ 0.8662, $\alpha_{D25°}$ —24.85°. α-Pinene was identified by means of the nitrosochloride melting at 103.0–103.5° and the nitrolpiperidine melting at 118°.

CAMPHENE—The fraction distilling at 160–164° and having $d_{15°}$ 0.8692, $\alpha_{D25°}$ —23.77°, weighed 22.7 g. (5.5 per cent). This oil was treated with glacial acetic acid-sulfuric acid mixture. On distilling the saponified oil with steam, the greater portion of the distillate came over as an oil. The small amount of solid isoborneol that formed in the condenser melted at 205–207° after one crystallization from petroleum ether.

β-PINENE—The greater portion of the original oil consisted of β-pinene, 205.5 g. (49.6 per cent) being collected between 164–170°. One hundred grams of oil boiling at 166–168° and having $d_{15°}$ 0.8680, $\alpha_{D24°}$ —21.16°, were oxidized with alkaline potassium permanganate. The crystalline sodium nopinate obtained yielded on acidification nopinic acid melting at 127°.

PHELLANDRENE—This terpene was found to be present in considerable amounts in the fractions boiling between 170–180°. The fraction boiling at 170–173° and having $\alpha_{D25°}$ —19.94° gave the largest yield of phellandrene nitrite, the latter melting at 102°.

DIPENTENE—Apparently, owing to the presence of considerable phellandrene, it was not possible to obtain a crystalline tetrabromide. The following fractions were examined: (1) b. p. 173–175°, $d_{15°}$ 0.8577, $\alpha_{D25°}$ —22.06°, weight 33.6 grams; (2) b. p. 175–180°, $d_{15°}$ 0.8577, $\alpha_{D25°}$ —21.85°, weight 19.8 g. By dissolving a portion of fraction (2) in dry ether and saturating with dry HCl gas it was possible to obtain dipentene dihydrochloride melting at 49°.

ESTER FRACTION—The fraction boiling at 205–235° was saponified with alcoholic potash. The oil recovered by steam distillation, having the rotation $\alpha_{D25°}$ —15.58°, was treated with a saturated solution of potassium permanganate until reduction of the solution ceased. On steam distillation a small amount of oil having a strong camphor odor was obtained, but the quantity was too small for further identification. The oxidation liquor was then filtered hot to remove manganese sludge and after cooling extracted with ether. The ether extract gave a little viscous oil having a cinnamon odor. The aqueous solution when acidified gave a copious crystalline precipitate that after sublimation melted at 183–184° and was identified as anisic acid. It is very probable that in this case, as well as in that of the needle oil of digger pine above, the anisic acid may be attributed to the presence of methylchavicol.

CADINENE—The fractions boiling between 265 and 284° were rich in cadinene, the oil having the rotation $\alpha_{D21°}$ +14.69°. The crystals obtained on treatment with HCl gas melted at 117–118° and had in ethereal solution the specific rotation $[\alpha]_D$—45.66° calculated from the following values:

$$\alpha = —1.375° \qquad p = 4.125$$
$$l = 1 \qquad d = 0.7300$$

LEAF AND TWIG OIL OF RED FIR (*Abies magnifica*, MURR.)

The oil examined had a light green color and a pungent, unpleasant odor. The physical and chemical constants are given in Table I.

The sample weighing 193 grams distilled as follows: 167–170°, 10 per cent; 170–181°, 47.5 per cent; 181–190°, 12.0 per cent; 190–236°, 9.0 per cent; 236–260°, 13 per cent.

FURFURAL—This aldehyde was qualitatively detected in the first fraction.

α-PINENE—By repeated fractionation 3.6 g. of oil were obtained which boiled at 160–164°. When treated with ethyl nitrite and hydrochloric acid an intense green coloration characteristic of the formation of pinene nitrosochloride developed, but no crystals deposited. There is little doubt that, with sufficient oil for a careful fractionation, the presence of α-pinene could be definitely established.

β-PINENE—The oil boiling at 164–168° had $\alpha_{D24°}$ —25.54°, $d_{15°}$ 0.8620, and yielded sodium nopinate on oxidation. The free nopinic acid melted at 126–127° which proved the presence of β-pinene. From 16–18 per cent of this terpene is present in the oil.

PHELLANDRENE—Phellandrene was the only terpene that could be detected in the fractions boiling above 168° and constitutes about 52 per cent of the original oil. The fraction boiling at 173–177°, $d_{15°}$ 0.8537, $\alpha_{D24°}$ —21.42°, gave a copious precipitate of phellandrene nitrite melting at 102–103°. Dipentene could not be detected as either the dihydrochloride or tetrabromide.

BORNEOL—Saponification of the fraction, boiling point 206–236°, followed by steam distillation yielded an oil. The oil was then oxidized and distilled with steam. The amount of solid camphor that collected in the receiver was too small for further investigation.

"GREEN OIL"—There were obtained between 255° and 260°, 22.3 g. of a deep green oil having the following properties: $d_{15°}$ 0.8963, $n_{D15°}$ 1.4952, specific rotation $[\alpha]_D$ —6.05°. When a drop of the oil was dissolved in glacial acetic acid and treated with bromine vapors the solution first turned purple, then deep blue. No crystalline derivative was obtained.

SUMMARY

The constituents present in the oils examined, with their approximate percentages, are the following:

Leaf and Twig Oils of Constituents Present	Digger Pine Per cent	Lodgepole Pine Per cent	Red Fir Per cent
Furfural	...	Trace	Trace
n-Heptane	3	...	...
l-α-Pinene	58–59	3	?
l-Camphene	...	5–6	...
l-β-Pinene	...	49–50	16–18
l-Phellandrene	...	19	52
Dipentene	...		0
l-Limonene	18	...	...
Bornyl ester (as acetate)	3.5	2	3.5
Free alcohol (as *l*-borneol)	6	7.5	7.5
Methylchavicol	?	?	...
"Green oil"	2–3	...	13
Cadinene	...	7	...
Losses by polymerization, etc.	9.5	6	6

FOREST PRODUCTS LABORATORY
FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE
(In Coöperation with the University of Wisconsin)
MADISON

THE ELECTROLYTIC SEPARATION OF ZINC, COPPER AND IRON FROM ARSENIC

By A. K. BALLS AND C. C. MCDONNELL

Received November 4, 1914

Satisfactory electrolytic methods for the quantitative separation of zinc and iron from arsenic have not been developed up to this time. With respect to the separation of copper from arsenic, several methods are in use, namely, in acid solution according to Freudenberg,[1] and in ammoniacal and cyanide solutions as first suggested by Smith and Frankel,[2] and McCay.[3]

The idea of separating arsenic from other metals by using an electrolyte of sodium or potassium hydroxide, although by no means novel, has not previously been developed to a workable basis except in the separation of tin and arsenic by Lampèn,[4] whose work seems to have been overlooked by more recent writers. A Fischer[5] says relative to separating zinc from arsenic that it has never been investigated and is only conceivable in an alkaline zincate solution with a definite voltage.

The precipitate formed on adding potassium or sodium hydroxide to the solution of a heavy metal is in the case of some metals soluble in an excess of the precipitant, forming a strongly alkaline solution from which the metal can be deposited by the electric current. Zinc and lead are examples of this, while arsenic, on the other hand, exists in solution as an alkaline arsenate or arsenite, and therefore travels toward the anode. With many metals, such as iron and copper, the precipitate is not dissolved by an excess of caustic alkali, but its formation may often be prevented by the action of certain organic substances, particularly citric and tartaric acids, and from these solutions the metal is easily deposited. Alkaline electrolytes are capable, therefore, of rather wide application.

In this paper we wish to describe the conditions which were found to give excellent results in the separation of arsenic from copper, from iron, and more especially from zinc. Some work is being done upon other metals, notably lead, but this is not yet ready for publication.

In all of these separations the arsenic must exist in the higher state of oxidation, otherwise a small quantity will be found in the cathode deposit, and some may also be volatilized.

ZINC FROM ARSENIC

It is necessary in connection with our official work in this laboratory to examine numerous samples of zinc arsenite and products containing it. It was in the course of investigations conducted on methods for analyzing these substances that the following experiments were undertaken.

The deposition of zinc from a caustic electrolyte in the absence of arsenic has been so fully discussed by others that we shall not take it up here except to say that we have found it entirely satisfactory.

Since a platinum electrode is injured by the deposition of zinc, the cathode used was a nickel dish, preferably with a surface which has been roughened either by etching or sand blasting. The experiments recorded here were very satisfactorily carried out in ordinary nickel crucibles of about 125 cc. capacity, offering to the deposit about 90 cm^2. of surface. The anode consisted of a No. 14 (B. & S.) platinum wire bent in the shape of a flat oval-shaped paddle, whose blade is about 2.5 × 2.0 cm., and suspended from the spindle of the rotating mechanism so that the paddle blade is just completely immersed in the liquid. This form of apparatus, besides being readily obtainable, has the advantage of permitting an unusually rapid agitation of the electrolyte.

PREPARATION OF SOLUTIONS—For the zinc solution a weighed amount of very pure zinc oxide[1] was dissolved in dilute sulfuric acid and made to a definite volume.

For the arsenic a solution of pure arsenic acid was used, which was standardized by the iodometric method described later.

Measured amounts of the zinc and arsenic solutions were mixed and sodium hydroxide or potassium hydroxide (50 per cent solution) added until the solution became clear, and then in excess to the extent of about 20 g. The solution was diluted to about 95 cc. and electrolyzed. The electrolysis was thus started at room temperature, but the liquid quickly became heated nearly to boiling.

It was found, as mentioned by Amberg,[2] that by using potassium hydroxide decidedly better zinc deposits were obtained than with sodium hydroxide. When sodium hydroxide was used, the deposit frequently showed a tendency to be spongy, although this could be remedied somewhat by increasing the rate of anode rotation. The presence of many organic substances in small quantities will also greatly increase the adherence of the deposit.[3] We found that glycerol and a mixture of equal parts of glycerol and alcohol worked very well in these experiments. Even alcohol alone had the same effect, but in this case a reddish brown resinous body was formed during the electrolysis. This did not vitiate the results, but rendered the siphonate more difficult to handle.

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[1] *Z. physik. Chem.*, **12** (1893), 117.

[2] *Amer. Chem. Jour.*, **12** (1890), 428.

[3] *Chem. Ztg.*, **14** (1890), 509.

[4] *Chemische Industrie*, **1907**, 128.

[5] *Electroanalytische Schnellmethoden*, **1908**, 246.

[1] The zinc oxide was analyzed by several methods with the greatest care and found to contain 99.84 per cent ZnO and 0.14 per cent moisture.

[2] *Ber.*, **36** (1903), 2489.

[3] Cf. Gmelin-Kraut, "Handbuch der anorg. Chemie," **4** (1), s. 559 *et seq.* (1911).

According to Amberg,[1] and Spear and Strahan,[2] nitrates should be absent. While we have found that the last trace of zinc is deposited very slowly in the presence of as little as 0.2 g. KNO_3, with such small quantities a particularly smooth and adherent deposit is obtained, and since the amount not deposited in a reasonable time should not exceed 0.5 mg., and is usually much less, this error is sometimes allowable. Consequently 0.1 to 0.2 g. of KNO_3 may be added to the solution in order to improve the quality of the deposit, without sensibly sacrificing accuracy, unless working upon small amounts of metal or small aliquots. In general, however, we prefer the use of potassium hydroxide, in which case the addition of any of these substances is unnecessary.

The most prolific source of error in all such determinations is undoubtedly in the weighing of the large dishes used as cathodes. The following procedure was found satisfactory. The weighings were made with two dishes, one of which was used always as a counterpoise. The dishes, which weighed approximately 70 g., were washed with absolute alcohol, dried in the air, heated for half an hour in an air oven at 110° and placed in a desiccator over sulfuric acid for at least an hour. They were then removed and weighed immediately. The zinc deposits, after the electrolytes had been siphoned out and replaced by distilled water, were washed well with absolute alcohol, dried in the air, heated in the oven at 110° and weighed as before. It is not necessary to use ether in drying the deposits, nor does any oxidation occur in the oven. Zinc deposits heated for 24 hrs. at a temperature of 140° C. did not show any change in weight.

The zinc was dissolved in strong nitric acid and tested for arsenic with ammonium molybdate. For comparison, similar tests were made on solutions containing known amounts of arsenic oxid. (0.1 mg. As_2O_5 was readily detected by this test). In many zinc deposits no arsenic at all was found and in no case did it exceed 0.2 mg.

Hydrogen sulfide was passed into the siphonates from several experiments and the amount of zinc shown to be present never exceeded 0.2 mg. (Such an amount of zinc in a liter of solution gives a distinct opalescence.)

DETERMINATION OF ARSENIC—The method employed for the determination of the arsenic was essentially that of Gooch and Browning[3] and was briefly as follows:

Evaporate the siphonate to about 200 cc. and acidify with sulfuric acid, adding 8 to 10 cc. of concentrated acid in excess. Then add 2 to 3 g. of potassium iodide, and boil down slowly until the volume is reduced to about 90 cc. Cool the solution and destroy the iodine remaining by adding sodium thiosulfate solution from a burette. Immediately add sodium bicarbonate in considerable excess, and titrate with standard iodine. Care should be taken not to continue the evaporation too far, as the large amount of alkali salts present may cause the solution to become superheated, with consequent loss of arsenious iodide.

Number 15 in Table I is the analysis of a commercial zinc arsenite. A two-gram sample was dissolved in sulfuric acid (1 to 5), made to 250 cc., caustic soda added to a 50 cc. aliquot, the arsenic oxidized by warming with a little sodium peroxide, and the solution electrolyzed. The results agreed with those obtained by standard gravimetric methods.

As lead and zinc are frequently found together in combination with arsenic, a few experiments were made to see what effect the lead would have on the procedure. In an alkaline solution lead separates out on the cathode. Cathodic lead tends to be spongy. Gartenmeister[1] has remedied this in an acid electrolyte by adding gallic or tannic acid. While we have found that the same substances will also make the deposit from an alkaline solution smooth, it is doubtful whether the deposited metal is free from organic impurities. If, however, the quantity of lead be quite small in comparison with the surface of the cathode (not more than 0.1 g. metal per 100 sq. cm.) the deposit will be satisfactory without the addition of any extraneous material. Cathodic lead also oxidizes so readily that it must be dried with the greatest care; but if a small quantity of lead is present with a larger amount of zinc, the lead deposits first and is subsequently coated by the zinc, which prevents its oxidation. The combined deposits are weighed, dissolved in dilute nitric acid and the lead determined electrolytically as peroxide.[2] If it is desired to determine directly the zinc, which will be in the siphonate from the PbO_2, this may be done by driving off the nitric acid and again using a caustic electrolyte to which about 5 g. of Rochelle salt have been added to hold up traces of nickel dissolved by the acid from the first cathode used.[3] Experiment 16 in Table I is an example of a determination of this kind. To obtain the best results a quantity of zinc at least equal to the lead should be present.

A description of the conditions employed and examples of the results obtained in separating zinc from arsenic are given in Table I.

IRON FROM ARSENIC

Iron deposits free from arsenic from a solution containing a large excess of caustic potash or soda in which precipitation of iron hydroxide has been prevented by previously adding tartaric acid.[4] The iron so obtained always contains carbon, unless the current is kept below 1.7 amperes per 100 sq. cm. If this is done, the amount of carbon present is negligible. The best results are obtained with a current density of less than 1 ampere per 100 sq. cm. With such a small current, however, the deposition is necessarily very slow, and the use of a rotating electrode unnecessary. It is often necessary to run such determinations over night. The iron may be in either the ferrous or ferric condition. The apparatus used was that described by Smith.[5] It consisted of an ordinary platinum dish cathode and

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[1] *Loc. cit.*

[2] THIS JOURNAL, **4** (1912), 889.

[3] *Am. Jour. Science*, **40** (1890), 66.

[1] *Chem. Ztg.*, **37** (1913), 1281.

[2] E. F. Smith, "Electroanalysis," 5th Ed., **1911**, p. 234.

[3] Cf. Vortmann, *Monats.*, **14** (1893), 536.

[4] Vortmann, *Loc. cit.*

[5] "Electroanalysis," 5th Ed., p. 42.

a spiral anode which could be rotated or not as desired.

In the experiments tabulated below the tartaric acid was added to the solution containing a known amount of pure Mohr's salt and a definite quantity of the arsenic acid solution, and this was poured into the caustic potash solution. If a precipitate is once allowed to form it can be redissolved only with the greatest difficulty. An excessive amount of sulfate is to be avoided, as sulfates of the alkalis are insoluble in strong caustic solutions. Occasionally, a deposit of iron oxide was observed at the anode but this can be prevented by the addition of a few cc. of alcohol. As a check on the purity of the deposit, in a number of cases the iron was dissolved in sulfuric acid, reduced with zinc, and titrated with potassium permanganate; and in other cases dissolved in hydrochloric acid and determined as ferric oxide.

TABLE I—SEPARATION OF ZINC FROM ARSENIC

Volume of Solution—95 cc.

	Grams Zn		Grams As_2O_5		Conditions of electrolysis				Electrolyte		
No.	Added	Found	Added	Found	Volts	Amps. ND_{100}	Time Min.	Anode rotation, R.P.M	Excess KOH Gms.	Excess NaOH Gms.	ADDITIONS
1	0.3000	0.2996	0.0500	0.0508	5.5	5.5	90	900	20	..	
2	0.1989	0.1992	0.0500	0.0498	4.5	4.4	60	800	20	..	
3	0.2984	0.2985	0.1968	0.1948	4.0	2.2	90	600	..	21	3 cc alcohol
4	0.2984	0.2986	0.1968	0.1965	4.5	4.0	70	700	..	21	3 cc. alcohol
5	0.2984	0.2983	0.1968	0.1962	4.5	3.2	75	600	..	21	2 cc. alcohol 2 cc. glycerol
6	0.2984	0.2980	0.2172	0.2163	4.0	2.2	90	800	20	..	2 cc. alcohol 2 cc. glycerol
7	0.2984	0.2990	0.2088	0.2102	4.6	4.4	45	900	20	..	0.2 gm. KNO_3
8	0.2984	0.2984	0.2088	....	4.2	3.1	60	700	20	..	0.2 gm. KNO_3
9	0.2984	0.2989	0.2172	0.2180	4.5	4.0	70	800	20	..	
10	0.2984	0.2984	0.2172	0.2178	4.5	4.0	70	800	20	..	
11	0.2000	0.2008	0.5000	0.4995	5.5	5.5	135	1000	20	..	
12	0.1989	0.1992	0.5000	0.5020	5.0	5.5	135	900	20	..	
13	0.1000	0.1004	0.5000	0.4992	4.5	4.4	120	900	20	..	
14	0.0995	0.0997	0.5000	0.5009	4.5	4.4	120	900	20	..	
15	0.1416(a)	0.1415	0.1054(b)	0.1053	4.0	2.0	60	600	..	15	5 gm. Na_2O_2
16	0.1989	0.1991	0.1968	0.1976	4.0	2.2	60	600	20	..	0.0717 gm. Pb added 0.0712 gm. recovered

(a) Determination (after removal of arsenic) as carbonate. See Treadwell (Hall), Vol. II, 3rd Ed., p. 142.
(b) Determination as pentasulfid. Neher, *Z. anal. Chem.*, **1893**, s. 45.

Many iron deposits were tested for arsenic in the same manner as the zinc deposits and more than 0.2 mg. of As_2O_5 was never found.

TABLE II—SEPARATION OF IRON FROM ARSENIC

Volume of Solution—100 cc

	Grams iron			Grams As_2O_5		Conditions of electrolysis				Electrolyte Grams	
No.	Taken	Found	Detd.	Taken	Found	Volts	Amps. ND_{100}	Time. Hrs.	Anode rotation, R.P.M.	Tartaric acid.	Excess KOH.
1	0.2000	0.1997	0.1998	0.0500	0.0508	1.2	0.4	18	0	3	20
2	0.2000	0.2009	0.1993	0.0434	0.0441	2.4	0.8	18	0	3	10
3	0.2000	0.1996	0.1986	0.1086	0.1084	1.8	0.5	18	0	3	20
4	0.3000	0.3011	0.2996	0.2172	0.2178	2.8	0.8	18	0	5	15
5	0.2000	0.1990	0.1992	0.1968	0.1968	2.8	1.7	$3\frac{1}{2}$	700	5	10
6	0.2000	0.2004	0.1990	0.1968	0.1968	2.8	0.8	11	0	5	10
7	0.2000	0.2007	0.2001	0.2172	0.2169	2.8	0.8	18	0	3	15
8	0.2000	0.2006	0.2000	0.2172	0.2181	2.5	1.3	18	0	3	20
9	0.2000	0.2011	0.1998	0.2172	0.2169	2.8	0.8	6	0	3	20
10	0.2000	0.1991	....	0.3932	0.3922	0.8	0.3	18	0	3	10
11	0.2000	0.2003	0.2007	0.3932	0.3928	0.8	0.3	13	0	3	10
12	0.2000	0.2002	0.1994	0.3932	0.3927	1.0	0.4	18	0	3	20
13	0.0800	0.0808	....	0.3932	0.3936	0.8	0.3	18	0	3	10
14	0.0800	0.0805	0.0800	0.3932	0.3932	0.8	0.3	20	0	3	20
15	0.0800	0.0806	0.0792	0.5000	0.4993	1.0	0.5	24	0	3	20

The arsenic was determined iodometrically as before. The presence of tartaric acid does not interfere with the titration.

Details of the method and results obtained are tabulated in Table II.

COPPER FROM ARSENIC

The same general method applies equally well to copper, the precipitation of hydroxide from the alkaline solution being prevented by tartaric acid. The copper separating from a caustic electrolyte tends to be spongy, and in order to get a firmly adherent deposit the anode is rotated quite rapidly (1000–1600 R. P. M.) and about two grams of potassium nitrate are introduced into the solution. The effect here seems to be, as with zinc, to decrease the rapidity of the decomposition while increasing the adherence of the deposit, but all the copper can be removed from the solution easily in a reasonable length of time.

The standard copper solution was prepared by dissolving a weighed amount of pure copper sulfate in water and making up to a definite volume. The copper content was verified by a number of electrolytic determinations in both nitric acid and potassium cyanide electrolytes. The arsenic solution was the same as that used in the work on zinc and iron.

The arsenic in the siphonate was determined iodometrically, as before.

The copper deposits were tested for arsenic with ammonium molybdate, as described previously, and they all showed less than 0.2 mg. of arsenic pentoxide.

The results obtained and details of the experiments are given in Table III.

In general, the successful carrying out of these separations depends principally upon having all the arsenic in the pentavalent form, upon the presence of a sufficient excess of alkali, and upon maintaining the conditions which produce an adherent deposit.

Should the arsenic be present in its lower form of oxidation it will invariably contaminate the deposit, and this will also occur, particularly in the case of iron, if too small an excess of alkali is used. A large excess is always advisable as it does not exert any harmful effect even when the electrolysis is unnecessarily prolonged. The voltage used does not, as far as we have experimented, have any important bearing on the results. Except in the case of iron, the current density may vary between wide limits; however, it occasionally happens that when too large, metallic arsenic will separate on the anode and finally appear in the solution. The time required for an electrolysis depends very largely on the amount of arsenic present, since the arsenates retard the deposition apparently in

Table III—Separation of Copper from Arsenic

Volume of Solution—100 cc.

	Grams Cu		Grams As_2O_5		Conditions of electrolysis				Electrolyte Grams		
No.	Taken	Found	Taken	Found	Volts	Amps. ND_{100}	Time. Min.	Anode rotation, R.P.M.	KNO_3.	Tartaric acid.	Excess KOH.
1	0.2061	0.2055	0.0434	0.0446	5.5	6.0	35	1200	1	1	20
2	0.2000	0.1992	0.0500	0.0508	4.5	4.0	40	1600	1	1	10
3	0.2061	0.2059	0.1086	0.1078	5.2	5.8	30	1100	1	1	20
4	0.2061	0.2065	0.1303	0.1307	3.6	4.0	40	1300	2	1	20
5	0.2065	0.2061	0.2088	0.2084	...	3.0	35	1000	1	1	20
6	0.2065	0.2064	0.2088	0.2088	4.0	4.0	30	1100	1	2	20
7	0.1993	0.1989	0.1968	0.1968	4.0	4.0	20	900	0	4	20
8	0.2065	0.2062	0.2088	0.2084	4.0	4.5	25	1100	1	1	20
9	0.2065	0.2063	0.2088	0.2090	4.0	4.0	30	1000	1	1/2	20
10	0.2000	0.2005	0.3932	0.3922	4.5	4.0	40	1560	1	1	10
11	0.2000	0.1994	0.3932	0.3934	4.8	5.0	40	1400	1	1	10
12	0.2000	0.2000	0.5000	0.4993	4.8	5.0	55	1400	1	1	10
13	0.0800	0.0806	0.3932	0.3948	4.5	4.0	30	1500	1	1	10
14	0.0800	0.0796	0.3932	0.3943	4.5	4.0	35	1500	1	1	10

much the same way as the nitrates. The drying of the deposits presents no special difficulty, but the weighings should be made with more than ordinary care.

CONCLUSION

Zinc, iron, copper, and small amounts of lead have all been successfully separated from arsenic in the electrolytic way by using an electrolyte containing a large excess of potassium or sodium hydroxide. The arsenic is determined in the solution from the electrolysis. Conditions have been worked out which insure good deposits, and we believe that the methods will often greatly simplify the course of analysis for many substances containing these metals.

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THE STANDARDIZATION OF ALKALIMETRIC SOLUTIONS

By Francis D. Dodge

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The text-book methods for determining the value of the acid and alkali solutions employed in volumetric analysis are not perfectly satisfactory as regards ease and convenience of manipulation. This will be admitted by most technical chemists, and will no doubt account for the numerous suggestions which have appeared in the chemical literature in recent years and which have as their object the simplification or improvement of known processes with respect to accuracy as well as convenience.

Any criticism of these methods is not in relation to accuracy of results, because in general that is merely a matter of manipulative skill; but, if one has convenience or economy of time in mind, it would seem that the amount of time and care required is disproportionate, or excessive, as compared with the theoretical simplicity of the end to be attained. Hence it is presumed that an account of some attempts made towards this very desirable simplification may be not without interest.

All methods so far proposed fall naturally into two classes which can be called direct and indirect. The direct methods involve the use of a standard pure substance, which can be weighed with all desirable accuracy and directly titrated. This appears to be the simplest and most desirable way, provided a thoroughly suitable standard substance can be found.

Of the indirect methods, the following may be noted:

PHYSICAL

Determination of specific gravity.

CHEMICAL

Gravimetric determination as $BaSO_4$, or AgCl.

Electrolysis of $CuSO_4$.

Evaporation with NH_3, and weighing $(NH_4)_2SO_4$.

Distillation of NH_3, etc.

Iodometric, involving the use of iodic acid and iodates, and thiosulfates.

Sodium oxalate, ignited to carbonate.

All these propositions are lacking in simplicity; under special conditions, some of them may, of course, be useful.

As already indicated, the value of a direct method will depend on the availability of the standard substance. A little consideration will show that the latter should comply as far as possible with the following specifications:

1—The standard should be *easily* obtained in a state of sufficient purity.

2—It should be *unalterable* in the air, at ordinary or moderately high temperatures, *i. e.*, neither hygroscopic nor efflorescent. Hence, hydrated compounds are, in general, undesirable.

3—It should be readily soluble in water and alcohol, thus allowing immediate titration in the cold.

4—It should have a high molecular, or equivalent weight, thus lessening the effect of small errors in weighing.

5—On titration, no interfering product, as carbonic anhydride, should be present.

6—The standard should be free from color, before and after titration, to avoid interference with indicators.

As far as the writer has been able to ascertain, no standard substance so far suggested answers perfectly these requirements.

Brief consideration and criticism of the degrees of approximation to the ideal exhibited by the compounds already proposed are presented below:

	Standard Substance	Equivalent weight	Fails to pass Specification No.					
	FOR ACIDS							
1	Sodium carbonate	53	1	2			5	
	Sodium metal	23		2		4		
	Magnesium metal	24	1			4		
	Borax	191		2				
	Calcium carbonate (Iceland spar)	50					5	
	FOR ALKALIES							
	Oxalic acid, anhydrous	45	1	2		4		
	hydrated	63	1	2		4		
	Acid oxalates	..	1	2				
	Succinic acid	59				4		
	Malonic acid	52	1			4		
	Benzoic acid	122			3			
	Phthalic acid	83			3			
	Phthalic anhydride	74			3			
	Salicylic acid	138			3			
	Nitro and amino acids	..	1					
	Picric acid	212						6
	Potassium bichromate	146						6
	Potassium bitartrate	188			3			
	Betain hydrochloride	153.5	1	2(?)				

The use of potassium acid tartrate has been strongly recommended by Borntraeger,[1] and the writer has obtained excellent results with it. Its purification is not exactly easy, but the main objection is its great

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[1] *Zeit. anal. Chem.*, **25**, 334.

insolubility in water and in alcohol, which makes the titration tedious. As an improvement on this, it seemed that an analogous compound might be more convenient as regards solubility, and the acid phthalates appeared worthy of examination.

The acid phthalate of potassium has not apparently been described. It is readily obtained by half-neutralization of a solution of phthalic anhydride and crystallizes nicely in hexagonal plates.

ACID POTASSIUM PHTHALATE

PREPARATION—50 g. resublimed phthalic anhydride are dissolved in about 200 cc. of water. The solution is exactly neutralized with a solution of about 60 g. of pure potassium hydroxide in an equal amount of water; 50 g. more of anhydride are then added, and the heating continued until all crystals are dissolved. The solution is now made up to about 550 g. with water, filtered hot, if necessary, and let cool, with continuous agitation to promote the formation of small crystals. When cold, the latter are filtered by suction or centrifuge. The yield is about 125 g. The product is recrystallized from 300 cc. of hot water and dried at 110°.

The salt is anhydrous $KHC_8H_4O_4$ with mol. wt. 204. It is soluble in 10 to 11 parts of water at ordinary temperatures, and in about 400 parts alcohol.

This compound seems to approximate the ideal substance, as shown by the following facts:

1—As regards purity, the sublimed anhydride is an admirable raw material and not expensive. Recrystallization of the salt is hardly necessary as the impurities derived from the alkali used should be minimal.

2—The salt is stable, anhydrous, not hygroscopic.

3—The solubility in water is sufficient.

4—The molecular weight is higher than that of any compound so far proposed, except picric acid.

5—It behaves like a monobasic acid, and can be titrated with all desirable sharpness.

6—It is colorless.

7—The writer has found it to work well in practice.

The acid phthalate of sodium was obtained by Wislicenus[1] as a by-product, and described as glassy, prismatic crystals, containing $2H_2O$. Salzer,[2] however, reports the salt as anhydrous. It is easily prepared in the manner described for the potassium salt, substituting sodium hydroxide or carbonate. In all cases, however, the writer found the fine transparent prisms to contain ${}^1/_2H_2O$. The salt is soluble in about 9 parts water at 25° and analyzed for moisture as follows:

Wt. of salt Grams	TREATMENT	Time Hrs.	LOSS IN WEIGHT	
			Gram	Per cent
5 (air dry)	Desiccator	115	0.0055	0.11
	Heated at 50° C.	24	0.0070	0.14
	Heated at 100–110° C.	12	0.2410	4.82
1.97 (air-dry)	Heated at 110° C.	12	0.0950	4.82
Moisture calculated for $NaHC_8H_4O_4.{}^1/_2H_2O$				4.57

The salt is thus fairly stable up to 50°; at 100–110° the crystals lose ${}^1/_2H_2O$ and become opaque, but retain their prismatic form. This anhydrous salt may be used as a standard, but the potassium salt seems preferable.

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[1] *Ann.*, **242**, 89.

[2] *Ber.*, **30**, 1496.

THE INFLUENCE OF HYDROXY ACIDS AND LACTONES UPON DETERMINATIONS OF THE CHEMICAL CONSTANTS OF FATTY ACIDS

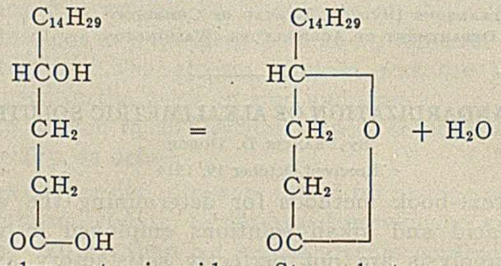
By C. A. BROWNE

Received October 6, 1914

The recent paper by Holland[1] upon "The Determination of the Acetyl Number of Oils, Fats, Etc.," recalls former discussions by Lewkowitsch, Benedikt and others regarding the value of the acetyl figure in the analysis of fatty acids. As the author has recently studied the determination of the acetyl number and other chemical constants in the insoluble acids of several decomposed butter fats, a few observations upon certain analytical data may possibly be of interest.

A serious difficulty, which often confronts the chemist in the analysis of fatty-acid mixtures, is the unstable character of the hydroxy-fatty acids. The latter, from their chemical behavior may be divided into two general classes: (1) the lactone-forming and (2) the non-lactone-forming hydroxy acids.

Lactone-forming hydroxy acids (more especially the γ acids) show a pronounced tendency, after being liberated, to form inner anhydrides. Thus γ-hydroxystearic acid, after separation from its salts or esters, passes immediately into stearo-lactone.



Hydroxy-stearic acid Stearo-lactone

The non-lactone-forming hydroxy acids, on the other hand, do not possess the property of yielding inner anhydrides. The hydroxyl group of this class of fatty acids remains unchanged and, in distinction from the hydroxyl group of the lactone-forming acids, is free to react with acetic anhydride during acetylation.

This difference in properties of the two classes of hydroxy-fatty acids has frequently been disregarded by chemists in their treatment of the subject. It is evident, however, that this factor must play at times an important part in the analysis of complex fatty acid mixtures.

INFLUENCE OF HYDROXY-FATTY ACIDS AND LACTONES ON DETERMINATIONS OF THE ACID, SAPONIFICATION AND ETHER NUMBERS

The insoluble acids prepared from the ordinary normal animal fats show usually but little difference between the acid and saponification numbers, the ether number in such cases being practically zero.

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[1] THIS JOURNAL, **6** (1914), 482.

In the case, however, of oxidized and decomposed fats, which contain hydroxy compounds, the formation of lactones in the mixture of fatty acids causes a depression in the acid number and an increase in the saponification and ether numbers. This can best be understood by taking a specific example.

Hydroxy-stearic acid, $C_{17}H_{34}OHCOOH$, of molecular weight 300.288 requires for neutralization and saponification 56.108 molecular parts of KOH. The milligrams of KOH necessary to neutralize and saponify 1 g. of hydroxy-stearic acid are then 56108 ÷ 300.288 = 186.85, the acid and saponification number.

If we take a mixture consisting of one molecular part of hydroxy-stearic acid and one molecular part of stearo-lactone the reaction upon neutralization with KOH would be

$$\underset{\text{Hydroxy-stearic acid}}{C_{17}H_{34}OHCOOH} + \underset{\text{Stearo-lactone}}{C_{17}H_{34}CO_2} + KOH$$
$$= \underset{\text{Potassium hydroxy-stearate}}{C_{17}H_{34}OHCOOK} + \underset{\text{Stearo-lactone}}{C_{17}H_{34}CO_2} + H_2O$$

In other words 582.560 molecular parts of the mixture would require for neutralization 56.108 molecular parts of KOH. The acid number of the mixture is then 56108 ÷ 582.560 = 96.31.

If we saponify the same mixture with KOH, the formula for the reaction would be

$$\underset{\text{Hydroxy-stearic acid}}{C_{17}H_{34}OHCOOH} + \underset{\text{Stearo-lactone}}{C_{17}H_{34}CO_2} + 2KOH$$
$$= \underset{\text{Potassium hydroxy-stearate}}{2C_{17}H_{34}OHCOOK} + H_2O$$

That is, 582.560 molecular parts of mixture would require for saponification 112.216 molecular parts of KOH. The saponification number of the mixture is then 112216 ÷ 582.560 = 192.62.

It is thus seen that if one-half of a sample of hydroxy-stearic acid should undergo lactonization the acid number would be depressed from 186.85 to 96.31 and the saponification number increased from 186.85 to 192.62. The original ether number of zero would become 192.62 — 96.31 = 96.31.

The occurrence of fatty acids which show a higher saponification than neutralization value has been frequently reported. Tortelli and Pergami[1] give a long list of fatty acids from various sources which show striking differences of this kind, these differences being usually found to increase with the age of the sample. Obviously with these differences in the acid and saponification numbers similar differences will be produced in the calculations of the mean molecular weights of the fatty acids.

Lewkowitsch[2] has also determined the acid and saponification numbers of mixed fatty acids and his results in general confirm the figures of Tortelli and Pergami. The general explanation of the differences, according to Lewkowitsch, is the occurrence of hydroxylated fatty acids which subsequently undergo dehydration with formation of lactones.

A few of the results obtained by Tortelli and Pergami and by Lewkowitsch are given in Columns I to V of Table I. Two determinations made by the author upon the insoluble acids of decomposed butter fat are also included for comparison.

Table I

Source of insoluble fatty acids	I Acid No.	II Mol. wt. from I	III Sapon. No.	IV Mol. wt. from III	V Diff. II–IV	Mol. wt. original lactone-free acids
TORTELLI AND PERGAMI						
Linseed oil—3 yrs.	191.5	292.8	205.4	273.2	19.6	274.4
Cottonseed oil—2 1/2 yrs.	194.3	288.7	204.5	274.3	14.4	275.3
Cherry kernel oil	191.3	293.2	213.7	262.5	31.7	264.4
Olive oil—3 yrs.	194.5	288.4	200.9	279.1	9.3	279.9
LEWKOWITSCH						
Tung oil	181.3	309.5	198.7	282.3	27.2	284.0
Peach kernel oil	196.8	285.0	205.0	273.6	11.4	274.4
Olive oil	200.9	279.2	200.9	279.2	0.0	279.2
Lard	196.0	286.2	205.1	273.5	12.7	274.4
BROWNE						
Butter fat—17 yrs.	211.3	265.5	219.6	255.5	10.0	256.3
Butter fat—17 yrs.	209.4	267.9	218.0	257.3	10.6	258.1

CALCULATION OF THE MEAN MOLECULAR WEIGHT OF INSOLUBLE FATTY ACIDS

The customary method of calculating the mean molecular weight of insoluble fatty acids by dividing 56108 by the acid number has caused many erroneous reports of this constant to appear in the literature. In the case of fatty acids which contain lactones the calculation of the mean molecular weight from the saponification number of the insoluble acids is much more accurate but is still incorrect since the weight of fatty acids taken for analysis has not been corrected for the loss in water which has resulted from formation of lactones. The correction for this loss in weight can be made as follows:

The ratio between the weight of water lost by formation of lactones and the weight of KOH required to saponify lactones is represented by

$$\frac{H_2O}{KOH} = \frac{18.016}{56.108} = 0.3211.$$

Let a be the acid number and s the saponification of a mixture of fatty acids; then the grams of KOH required to saponify the lactones in 1 g. of fatty acids equal $0.001\ (s - a)$ and the weight of water lost by dehydration is $0.0003211\ (s - a)$. The saponification number of the fatty acids before lactone formation would then be $\dfrac{s}{1 + 0.0003211\ (s - a)}$ which divided into 56108 would give the mean molecular weight (m) or

$$m = \frac{56108 + 18.016\ (s - a)}{s}$$

It was by this formula that the molecular weights of the original lactone-free acids in Table I were calculated. While the values thus found do not greatly differ from those calculated from the saponification numbers there might arise instances where the errors by the latter method would be of considerable importance.

INFLUENCE OF HYDROXY ACIDS AND LACTONES ON DETERMINATION OF THE ACETYL NUMBER

It was one of the services of Lewkowitsch to call the attention of chemists to the necessity of determining the acetyl constant of fatty acids by a direct estimation of the acetic acid. He showed that the original method of Benedikt and Ulzer, by which the acetyl number was estimated by taking the difference

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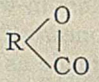
[1] L'Orosi, **1901**, 1; Lewkowitsch, "Oils, Fats and Waxes," 4th Ed., Vol. 1, pp. 419–421.

[2] Lewkowitsch, "Oils, Fats and Waxes," 4th Ed., Vol. 1, p. 421.

between the acid and saponification numbers of the acetylated fatty acids, usually gave too high results. This error was explained by Lewkowitsch as being due to the conversion of a part of the fatty acids during acetylation into anhydrides of the general formula $(RCO)_2O$: the latter by not becoming completely hydrolyzed during the subsequent washing cause a depression in the acetyl-acid number with a consequent increase in the acetyl-ether number. As examples of the effects of anhydride formation Lewkowitsch[1] states that he obtained the following acetyl values: palmitic acid 82.6, stearic acid 82.29, capric acid 174.00, lauric acid 132.49. These high results, however, must have been due to some unusual condition of acetylation as no such values are obtained under the conditions described by Benekidt and Ulzer for their method.

The errors of estimating the acetyl constant of fatty acids by taking the difference between the acid and saponification numbers of the acetylated acids were also recognized by Benedikt and Ulzer.[2] These authorities took the view, however, that, since fatty acids which contained no hydroxyl groups showed practically the same acid number before and after acetylation, the formation of fatty anhydrides of the formula $(RCO)_2O$ was not the real cause of the error. Benedikt and Ulzer attributed the discrepancies rather to the formation during acetylation of inner anhydrides or lactones of the general formula  $R\left\langle\begin{matrix}O\\ |\\ CO\end{matrix}\right.$, which would cause a decrease in the acetyl-acid number and an increase in the acetyl-ether number. Since, however, this increase in the acetyl-ether number is due primarily to hydroxy acids which have undergone lactonization, the acetyl-ether number would still remain a fairly accurate measure of the hydroxy acids which were originally present.

As for the lactones which might occur in the mixed fatty acids and would also cause an increase in the acetyl-ether number, Benedikt and Ulzer[3] subtract the ether number due to such lactones from the acetyl-ether number and call the remainder the true acetyl number (Reine Acetylzahl).

A clearer idea of the various questions involved may be secured if we take again the previous example of an equimolecular mixture of hydroxy-stearic acid and stearo-lactone. The action of acetic anhydride upon such a mixture would be

$$C_{17}H_{34}OHCOOH + C_{17}H_{34}CO_2 + (CH_3CO)_2O$$

Hydroxy-stearic acid Stearo-lactone Acetic anhydride

$$= C_{17}H_{34}OCH_3COCOOH + C_{17}H_{34}CO_2 + CH_3COOH$$

Acetoxy-stearic acid Stearo-lactone Acetic acid

When the acetylated acids are neutralized with KOH, as in the determination of the acetyl acid number, the reaction proceeds as follows:

$$C_{17}H_{34}OCH_3COCOOH + C_{17}H_{34}CO_2 + KOH$$

Acetoxy-stearic acid Stearo-lactone

$$= C_{17}H_{34}OCH_3COCOOK + C_{17}H_{34}CO_2 + H_2O$$

Potassium acetoxy-stearate Stearo-lactone

624.576 molecular parts of acetylated mixture require for neutralization 56.108 parts of KOH. The acetyl-acid number of the mixture would then be 56108 ÷ 624.576 = 89.83.

In case the acetylated mixture be saponified with an excess of KOH the reaction would be

$$C_{17}H_{34}OCH_3COCOOH + C_{17}H_{34}CO_2 + 3KOH$$

Acetoxy-stearic acid Stearo-lactone

$$= 2C_{17}H_{34}OHCOOK + CH_3COOK + H_2O$$

Potassium hydroxy-stearate Potassium acetate

The acetyl-saponification number of the acetylated mixture would then be 168324 ÷ 624.576 = 269.50.

The acetyl-ether number (acetyl number of Benedikt and Ulzer) is then 269.50 — 89.83 = 179.67.

The acetyl number of Lewkowitsch, *i. e.*, the mg. of KOH necessary to saponify the combined acetyl would be 56108 ÷ 624.576 = 89.83.

The relationship of the theoretical constants for the non-acetylated and acetylated mixture of hydroxy-stearic acid and stearo-lactone is shown in Table II:

TABLE II

Hydroxy-stearic acid and stearo-lactone	Acid No.	Sapon. No.	Ether No.	Acetyl No.	Lactone No.
Non-acetylated	96.31	192.62	96.31	...	96.31
Acetylated	89.83	269.50	179.67	89.83	89.83

The acid number of the acetylated mixture is lower and the ether and saponification numbers are higher than the similar constants of the non-acetylated product.

The lactone number, *i. e.*, the mg. of KOH necessary to saponify the lactones in 1 g. of acids is lower in the acetylated mixture.

If we subtract the ether number of the non-acetylated from the ether number of the acetylated mixture we obtain 83.36—the so-called "Reine Acetylzahl" of Benedikt and Ulzer; this value, owing to the noncorrection for increase in weight of the fatty acids during acetylation, is less than 89.83—the true acetyl number of Lewkowitsch.

Theoretically, the increase in weight of fatty acids during acetylation is expressed by the ratio of the acid number of the non-acetylated divided by the acid number of the acetylated acids.

Let a be the acid no. of the non-acetylated acid.

Let α be the acid no. of the acetylated acid.

Let s be the saponification no. of the non-acetylated acid.

Let σ be the saponification no. of the acetylated acid.

Let e be the ether no. of the non-acetylated acid.

Let ϵ be the ether no. of the acetylated acid.

Let x be the acetyl no. on basis of non-acetylated acid.

Let ξ be the acetyl no. of the acetylated acid.

The ratio of KOH used in saponifying acetyl to the increase in weight of fatty acids during acetylation is expressed by:

$$\frac{C_2H_2O}{KOH} = \frac{42.016}{56.108} = 0.7488$$

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[1] Lewkowitsch, *J. Soc. Chem. Ind.* (1890), p. 660.

[2] Benedikt-Ulzer, "Analyse der Fette," 3rd Ed. (1897), p. 179.

[3] Benedikt and Ulzer, "Analyse der Fette," 3rd Ed. (1897), p. 650. In the sentence "Davon ist die constante Verseifungszahl in Abzug zu bringen" Verseifungszahl is obviously a misprint for Aetherzahl.

If x be the true acetyl number on the basis of the non-acetylated acids, the g. of KOH necessary to saponify the acetyl after acetylating 1 g. of mixed acids would be $0.001x$. The weight of the 1 g. of acids after acetylating would then be $1 + 0.0007488x$.

Then

$$\frac{x}{1 + 0.0007488x} = \xi$$

$$\text{and } x = \frac{\xi}{1 - 0.0007488\,\xi} \qquad \text{I}$$

$$\frac{a}{1 + 0.0007488\,x} = \alpha \qquad \text{II}$$

Substituting I in II we obtain

$$\xi = \frac{a - \alpha}{0.0007488\,a} \qquad \text{III}$$

The small denominator in Formula III causes a very great multiplication of any experimental errors. The following methods of calculation are less objectionable.

Theoretically, the lactone number of the acetylated acids equals $\frac{e\alpha}{a}$, then the acetyl number of the acetylated acids is found by the equation

$$\xi = \epsilon - \frac{e\alpha}{a} \qquad \text{IV}$$

Since $e = s - a$ and $\epsilon = \sigma - \alpha$, we obtain by substituting these values for e and ϵ in Equation IV

$$\xi = \sigma - \frac{s\alpha}{a} \qquad \text{V}$$

The determination of the acetyl number in the insoluble acids of two decomposed butter fats was carried out by the author both according to the original Benedikt-Ulzer method and the improved method of Lewkowitsch. The determinations were all made upon the same weighed sample of acetylated acids.

After determining the acetyl acid and acetyl-saponification numbers, the calculated amount of standard acid was added to unite with all the alkali combined as potassium soaps. The insoluble acids were filtered off and the free acetic acid in the filtrate determined by titration.

The insoluble acids from the determination of the acetyl numbers were washed with boiling water, dried, and the acid and saponification numbers of the de-acetylated product determined. A summary of the results is given in Table III.

TABLE III—INSOLUBLE FATTY ACIDS FROM BUTTER FATS

No.		Acid No.	Sapon. No.	Ether No.	Acetyl No.	Lactone No.
1	Non-acetylated..........	211.32	219.59	8.27	...	8.27
1	Acetylated..............	194.71	238.88	44.17	37.04	7.13
1	De-acetylated...........	201.52	209.13	7.61	...	7.61
2	Non-acetylated..........	209.45	218.02	8.57	...	8.57
2	Acetylated..............	196.21	238.65	42.44	35.72	6.72
2	De-acetylated...........	205.00	212.35	7.35	...	7.35

The same relationship is noted between the constants of the non-acetylated and acetylated acids as between the theoretical constants of Table II.

It will be instructive to compare the acetyl numbers actually determined with the numbers calculated by Formulas III and IV.

The calculation from the acid numbers of the non-acetylated and acetylated acids, using Formula III, gives for Sample 1 an acetyl number of 105.00 and for Sample 2 an acetyl number of 84.40. These calculated values, which are several times those actually found, show a depression in the acid number of the acetylated acids greater than that, due to the increase in weight from acetylation, a depression of 1 in the acid number making a difference of about 7 in the acetyl number as thus calculated.

This excessive depression of the acid number of the acetylated acids, as already stated, was explained by Lewkowitsch as being due to the formation of fatty anhydrides, and by Benedikt and Ulzer as being due to the formation of lactones. There is, however, one other possibility, and that is the decomposition of some of the fatty acids during acetylation. Table III shows that the constants of the de-acetylated acids are uniformly lower than those of the acids before acetylating and this would indicate the formation of small amounts of decomposition products by the boiling acetic anhydride. The much darker color of the de-acetylated acids is an additional indication of such decomposition. If the formation of fatty anhydrides or lactones were the sole cause of the depression in the acetyl-acid number, the constants of the de-acetylated and non-acetylated acids should agree.

If the calculation of the acetyl number be based upon the acid numbers of the de-acetylated and acetylated acids we obtain, using Formula III, for Sample 1 an acetyl number of 45.06 and for Sample 2 an acetyl number of 57.26. The values thus calculated approach much nearer those actually found; there still remains, however, a marked discrepancy which may be due to the dehydration of a small amount of fatty acids during acetylation with formation of anhydrides or lactones.

If the calculation of the acetyl number be based upon the ether or saponification numbers, using Formulas IV or V, experimental errors are less magnified than by use of Formula III and a much closer agreement in the results is obtained.

	Lactone No.		Acetyl No.	
	1	2	1	2
From ether no. of non-acetylated acids..........	7.62	8.03	36.55	34.41
From ether no. of de-acetylated acids...........	7.36	7.03	36.81	35.41
Direct determination..........................	7.13	6.72	37.04	35.72

As was the case with Formula III, the calculations from the constants of the de-acetylated acids agree more closely with the actual determinations than the calculations from the constants of the non-acetylated acids.

A comparison of the lactone numbers shows the determined values to be lower than those calculated, whereas if lactones or anhydrides were formed during acetylation the determined lactone values might be expected to be higher. The contradiction may perhaps be due to the fact that some of the lactones in the fatty acids exist in an unstable δ or other form, and by the action of the acetic anhydride become acetylated with the hydroxy acids; these decomposed lactones during the drying of the de-acetylated acids might again be reformed in whole or in part. In confirmation of this view it might be mentioned that Lewkowitsch[1] obtained pronounced acetyl values with certain substances of a lactonic nature. The discrepancies, however, in view of the limitations which attend an indirect method of calculation, are not great enough to warrant making any sweeping conclusions. Further investigations upon the fatty acids from other sources are needed before this and other doubtful points can be decided. Changes during acetylation through the partial destruction of fatty acids, through the formation of small amounts of fatty anhydrides or lactones, and through the slight acetylation of preexisting lactones, may, however, be considered as among the possible causes of disturbances in the normal process of acetylation.

Finally, it must be admitted that there is much truth in the argument that, since the lactones in a mixture of fatty acids are derived from preexisting hydroxy acids, the acetyl number of Benedikt-Ulzer is a truer measure of the original hydroxyl content of fatty acids than the acetyl number of Lewkowitsch. Thus γ-hydroxy-stearic acid in the glyceride molecule can be acetylated and would show an acetyl number by the method of Lewkowitsch, whereas, the separated fatty acids would show no acetyl number on account of the formation of stearo-lactone.

The acetyl value of a mixture of fatty acids may be calculated back to the condition preceding lactone formation in the following way:

The ratio between KOH used to saponify lactones and the increase in weight which the acids would undergo from acetylation of lactones is represented by

$$\frac{C_2H_4O_2}{KOH} = \frac{60.032}{56.108} = 1.07$$

Let ϵ and ξ be respectively the acetyl-ether and true acetyl numbers, then $\epsilon - \xi$ = the lactone number and $0.001\ (\epsilon - \xi)$ = the g. of KOH required to saponify the lactones in 1 g. of acetylated acids. $1.07 \times 0.001\ (\epsilon - \xi) = 0.00107\ (\epsilon - \xi)$ = the increase in weight of 1 g. of acetylated acids if the lactones present were also acetylated.

The original acetyl number, calculated to the acetylated hydroxy acids before lactone formation, then

$$= \frac{\epsilon}{1 + 0.00107\ (\epsilon - \xi)}.$$

In the author's experience a combination of the Benedikt-Ulzer and Lewkowitsch methods for determining the acetyl number has been found to throw most light upon the chemical changes which have taken place in insoluble fatty acids as a result of oxidation. The determinations of acid, saponification, ether, acetyl and lactone numbers can all be performed upon one weighed sample of acetylated acids and the results enable the chemist to estimate the relative distribution of the free and lactonized hydroxy acids.

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[1] Lewkowitsch, *Analyst* (1899), 339.

A NEW METHOD FOR THE DETERMINATION OF UNSAPONIFIABLE MATTER APPLICABLE TO ETHER EXTRACTS, FATS, OILS AND WAXES[1]

By J. B. Rather[2]

Received October 27, 1914

Methods for the removal of unsaponifiable matter from fats and oils fall into two divisions:[3] (1) Extraction of the soap solution with solvents, and (2) the extraction of the dried soap with solvents. The method here proposed differs from both of these general processes in that the fatty acids are removed from the unsaponified material by precipitation from ethereal solution.

Stellwaag[4] in his work on the unsaponifiable matter in concentrated feeding stuffs and Fraps and Rather[5] in their investigation on the unsaponifiable matter in hays have shown the need of a rapid and reasonably accurate method for the systematic removal of unsaponified matter in the determination of fats.

PRECIPITATION METHOD

The method used for the determination of unsaponifiable matter in ether extracts was adopted after considerable experimental work. The data on which it is based will be published in another place.[6] The process, designated as the Precipitation Method, is as follows: Add 20 cc. of approximately 2 *N* alcoholic sodium hydroxide to a known amount of the sample (about 0.4 g.), and boil under a reflux condenser for one hour. Evaporate nearly to dryness and add 3.5 cc. glacial acetic acid, or its equivalent in weaker acetic acid. Add 50 cc. of redistilled ether and warm to dissolve the extract. Add 25 cc. water and warm a minute more. Transfer to a 500 cc. pear-shaped separatory funnel with a short neck and wash out the flask with 5 successive 20 cc. portions of ether, pouring the washings in the funnel. Turn the funnel on its side and shake gently. The two layers should now be clear and the aqueous layer nearly colorless. Draw off the lower layer into a 500 cc. Erlenmeyer flask. Add to the ethereal solution 10 cc. of warm 1 : 2 aqueous sodium hydroxide solution, turn the funnel on its side and shake gently. Allow the precipitate to settle, add 25 cc. warm water, hold funnel in vertical position and give rotary motion. Allow the two layers to separate, and draw off the clear aqueous solution into the Erlenmeyer flask, leaving any emulsion in the funnel. Repeat and then shake gently as above with 5 successive 30 cc. portions of cold water, allowing a short time for the two solutions to separate, and add the washings to the soap solution in the Erlenmeyer flask. Transfer the ethereal solution to a tared 200 cc. flask, evaporate or distil off the ether, and dry to constant weight in a steam oven at 100° C.

The following correction for fatty acids in unsaponified should be used for material high in fatty acids and low in unsaponified. Add 20 cc. of 0.2 *N* hydrochloric

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[1] Abstracted by the author from Texas Experiment Station, *Bull.* **169.**

[2] Under the general direction of G. S. Fraps, Chemist.

[3] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., Vol. I, p. 456–60.

[4] *Landw. Versuch. Stat.*, **37**, 148.

[5] Texas Exp. Sta., *Bull.* **150.**

[6] *Loc. cit.*

acid to the ethereal solution of the unsaponified matter in the separatory funnel before evaporation, stopper and shake vigorously. Draw off the aqueous layer and discard. Evaporate the ethereal solution, dry and weigh. Heat to boiling with 20 cc. alcohol, titrate with *N*/10 sodium hydroxide and phenolphthalein, running a blank on the alcohol. Multiply the corrected reading by 0.028. The result is grams fatty acids in the unsaponified matter. Subtract this from the unsaponified matter. The amount of fatty acids dissolved in the ethereal solution of unsaponified matter is, on an average, 16 mg. for substances very low in unsaponified matter and this figure may be used if very accurate results are not desired. The amount of fatty acids in unsaponified fractions from samples containing 25 per cent or more of unsaponified may be disregarded. It amounts to about 2 mg. on an average and is balanced by a corresponding amount of unsaponified matter in the soap solution.

The results on a number of ether extracts from plant and animal products are given in Table I, together with results by the method of Fraps and Rather[1] (Digestion Method).

TABLE I—UNSAPONIFIED MATTER IN ETHER EXTRACTS

	Method	Precipitation		Digestion	
No.	Percentage of	Extract	Sample	Extract	Sample
1	Wheat shorts	6	0.23	6	0.23
2	Corn chops	4	0.16	6	0.25
3	Cottonseed meal	3	0.47	2	0.28
4	Rice bran	8	0.60	2	0.18
5	Milo maize chops	7	0.21	4	0.13
6	Cold pressed cottonseed	4	0.29	2	0.16
7	Kafir chops	8	0.26	17	0.56
8	Corn bran	3	0.29	..	....
9	Red rice	9	0.15	9	0.14
10	Wheat bran	6	0.25	4	0.18
11	Wheat shorts	6	0.17	3	0.07
12	Rice polish	0.5	0.51	0.5	0.19
13	Tobasa grass	61	0.56	36	0.33
14	Sheep excrement from No. 13	66	0.70	47	0.50
15	Prairie hay	37	0.84	46	1.05
16	Sudan grass	38	0.55	36	0.53
17	Excrement from No. 15	59	1.68	63	1.78
18	Excrement from No. 16	74	1.41	69	1.32
19	Sudan straw	38	0.55	30	0.43
20	Sorghum hay	27	0.49	32	0.58
21	Excrement from No. 19	64	1.09	69	1.18
22	Moth bean hay	43	0.66	47	0.73
23	Excrement from No. 20	61	1.08	45	0.80
24	Excrement from No. 22	66	1.99	58	1.76
	Average concentrates	5	0.30	5	0.22
	Average, hays and excrements	53	0.97	50	0.92

The results are expressed in percentage of extract and in percentage of sample. The digestion method, as already reported,[2] was devised because the ordinary methods for the removal of unsaponified material from ether extracts very rich in that substance proved inadequate. The method is very long, but it gave satisfactory results with hays and fodders. On applying it to extracts consisting almost entirely of fats, the method was found to be very tedious. The precipitation method described herein was found to be equally as applicable to extracts rich in fat as to those poor in fat. It is a very rapid method and the process is not attended with any difficulty. The results obtained by this method were, as a rule, about the same as by the digestion method.

The ether extracts of the concentrated feed-stuffs examined contained an average of 5 per cent unsaponifiable matter in percentage of extract and 0.30 per cent in percentage of sample. The error introduced by estimating this material as fat amounts to 0.50 per cent (on sample) or more in the cottonseed meal, rice bran and rice polish. With the hays and excrements the great need of a more reliable method for the estimation of fats is shown by the amount of unsaponifiable matter obtained. This varied, in the samples examined, from 27 to 74 per cent of the extract and from 0.49 to 1.99 per cent of the sample. These results confirm those previously reported from this laboratory.

The precipitation method proposed in this article is believed to be very rapid and accurate, and to furnish a very complete separation of the unsaponified matter from the saponified material in ether extracts, fats, oils and waxes.

SUMMARY

A method for the removal of unsaponifiable matter from ether extracts has been devised, which is applicable to materials both rich and poor in unsaponifiable matter. The method is believed to have several points of superiority over others which have been proposed.

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COLLEGE STATION, TEXAS

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[1] Texas Exp. Sta., *Bull.* **150.**

[2] *Loc. cit.*

DETERMINATION OF FORMIC ACID IN KETCHUP

By C. A. PETERS AND L. P. HOWARD

Received October 24, 1914

This work was undertaken to find out whether formic acid can be determined readily and quantitatively, if present in ordinary ketchup.

The process in brief consisted in passing steam under pressure through a sample of ketchup in a flask, in allowing the material carried from the ketchup to be in contact with a suspension of calcium carbonate in a second flask, and in determining the soluble formate in the filtrate from the calcium carbonate suspension.

The ketchup used was a sample of "Blue Label" purchased at a local store, said to contain 0.1 per cent of sodium benzoate,[1] to which formic acid was added as desired. The method for the estimation of the formic acid was the gravimetric method described by Fincke.[2]

To obtain steam for nearly all the work, a connection was made with a heating radiator. To assure intimate mixing of the distillate in the second flask with the suspension of calcium carbonate, the hydra-headed tube, described by Stolzenberg,[3] was used except that the tube had only six openings, whereas Stolzenberg specifies eight. The openings were of 0.5 to 1.0 mm. in diameter. For both flasks we used long neck 500 cc. Kjeldahl's, those with wide openings being selected to admit the variously bent tubes.

In a few distillations, where the steam supply was taken at some distance from its source, the condensation of water in the flask containing ketchup was so great that a third flask had to be placed between the steam supply and the flask containing the ketchup to catch the condensed water.

Some preliminary experiments were necessary to

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[1] *Zeit. Nahr. Genussm.*, **22** (1911), 98. Fincke here states that benzoic acid does not reduce mercuric chlorid.

[2] *Zeit. Nahr. Genussm*, **21** (1911), 5.

[3] *Chem. Ztg.*, **32** (1908), 770.

ascertain the conditions under which the determination could be carried out. To see if the steam or reagents used contained substances that would reduce mercuric chloride, steam was passed through the apparatus for one and one-half hours until 1000 cc. of distillate had collected. The filtrate from the calcium carbonate suspension was evaporated to a small volume, and allowed to act on mercuric chloride with the addition of a few grams of sodium chloride and sodium acetate (the latter to neutralize the hydrochloric acid formed during the reaction). After eliminating several samples of acetate and acetic acid, which contained considerable amounts of reducing substances—Fincke[1] states that most acetic acid contains formic acid—the amounts of reduced mercurous chloride corresponded to only 0.2 to 0.4 mg. of formic acid, an amount which was accepted as a constant error in the process with the reagents at hand.

Experimentation with various amounts of ketchup in the first 500 cc. Kjeldahl flask established the fact that 40 g. of ordinary ketchup in 100 cc. of water could be subjected to a vigorous action of steam without serious danger of spattering. Inclining the flask at an angle of 45°, keeping the outlet tube at the top, reduced this danger. A piece of paraffin, as large as half a pea, also helped to reduce the frothing. Larger amounts of ketchup than 40 g. in 100 cc. of water made spattering a difficulty, some colored material being carried over into the suspension of calcium carbonate.

The time necessary to volatilize formic acid in this apparatus was next subjected to test. An amount of formic acid equal to 0.0405 g. was placed in 100 cc. of water in the first Kjeldahl flask ultimately intended to receive ketchup. One gram of precipitated calcium carbonate in 100 cc. of water was placed in the second flask and steam passed through for various lengths of time, flames under each flask being adjusted so that the volumes remained constant. After 50 minutes, 80 per cent of the formic acid in the first flask was held by the calcium carbonate in the second flask, and in one and one-half hours 91.6 per cent of the formic acid was held by the suspension.

Steam was next passed through 41 g. samples of ketchup acidulated with 0.5 g. of tartaric acid to determine if material capable of reducing mercuric chloride would be caught by the suspension. The filtrates from the calcium carbonate gave at first up to 6 mg. of suspended matter after treatment with mercuric chloride. It was evident at a glance that the light brown flocculent precipitate was not calomel. Filtering the solutions through paper before adding the mercuric chloride reduced the amount of the precipitate subsequently appearing to 0.3 to 0.8 mg. calculated as formic acid. The character of this precipitate was not investigated, and it was considered that the amounts of reducing substances volatilized from ketchup by steam and acting upon calcium carbonate, other than the 0.2 to 0.4 mg. introduced in the reagents, were negligible.

If new rubber stoppers are used in the flasks during the reduction of the mercuric chloride the stoppers should be boiled in caustic soda to remove the loosely adhering sulfur, some of which might otherwise be weighed as mercuric chloride.

The data collected in these preliminary experiments just described enabled us to adapt the method of Fincke to the determination of formic acid in ketchup. The reagents used and details of the process follow.

REAGENTS—Mercuric chloride solution: 100 g. per liter containing 30 g. sodium chloride.[1] Sodium acetate: 300 g. per liter. Acetic acid and acetate should be free from formic acid. Tartaric acid: 100 g. per liter.

PROCESS—About 40 g. of ketchup were weighed out and washed into a 500 cc. wide mouth, long neck Kjeldahl flask to which was added 0.5 g. of tartaric acid. This flask was supported at an angle of 45° and steam passed through it for one and one-half hours. Volatile matter from the flask was forced through a Stolzenberg tube, adjusted in the second Kjeldahl flask of 500 cc. capacity, containing 1.0 g. of precipitated calcium carbonate. Material distilling from the calcium carbonate suspension passed through a Liebig condenser. The volume in both flasks was kept at 100 cc. by regulation of the flame underneath. When 1000 cc. of distillate had been collected (which took one and one-half hours with our apparatus) the steam was shut off—it was found desirable to insert a T-tube, closed with a pinch-cock, in the system to quickly adjust the pressure. The contents of the flask containing the calcium carbonate were then filtered and well washed with hot water, and the filtrate was evaporated on a steam bath to a volume of 20 to 50 cc. If any precipitate appeared in the liquid it was filtered; otherwise it was transferred into a 300 cc. Erlenmeyer flask to which 5 to 20 cc. of mercuric chloride[2] and 5 to 10 cc. of sodium acetate[2] solutions were added. The flask was stoppered with clean rubber stoppers, carrying 2 feet of glass tubing to act as air condensers and was inserted in the hot water of a steam bath. The larger rings of the bath were put over the flask, so that all the liquid was under water and some of the air space above was not exposed to steam. After two hours' heating the precipitate was filtered on weighed Gooch crucibles previously dried at 100°, and washed with hot water, alcohol and ether in the order named, dried at 100° for three-quarters of an hour, cooled and weighed. The weight of calomel multiplied by 0.0975 gave the weight of formic acid.[3] Results obtained by this method are given in the following table:

DISTILLATION OF FORMIC ACID IN KETCHUP

No.	1	2	3
Formic acid used—grams	0.0405	0.0405	0.0405
Time of distillation—minutes	80	90	120
Formic acid recovered from calcium carbonate suspension—per cent	89.5	91.6	91.9

SUMMARY

It is evident that by applying the Fincke process,

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[1] *Loc. cit.*, p. 2.

[1] Fincke states that sodium chloride prevents the formation of insoluble compounds between mercuric chloride and salicylic acid.

[2] The amount of mercuric chloride is 15 times the amount of formic acid present, while 3 g. of sodium acetate are necessary when the largest amounts (125 mg.) of formic acid are present.

[3] *Z. Nahr. Genussm.*, **25**, 386.

with the apparatus described above, 91 to 92 per cent of the total formic acid added to ketchup can be collected in an hour and a half, when the amount of distillate that has passed through the apparatus is about 1000 cc.

Thanks are due Mr. H. C. Lythgoe, chemist of the State Board of Health Laboratory of Massachusetts, for the suggestion which led to this work.

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THE VOLUMETRIC FEHLING METHOD USING A NEW INDICATOR

By A. M. BRECKLER

Received October 21, 1914

The volumetric Fehling method has been looked on very unjustly as inaccurate and unreliable. An inspection of the work of A. W. Peters[1] shows that under the most carefully controlled conditions of the gravimetric method, the ability to duplicate reducing sugar determinations is limited to an accuracy of about one part in 200. His dextrose copper ratios fluctuate about a mean value of 0.522 in the range of 25 to 100 mg. of dextrose. The highest value is 525 and the lowest is 520, the value in each case being a mean of 4 to 6 determinations. The work of Munson and Walker[2] at times shows departures from the average which are fully as great. In seeking a method of reducing sugar estimation, therefore, an accuracy of one part in 200 is as great as can be expected.

The method here described is dependent on a constant volume at the close of the titration, a constant time of boiling, and the use of sodium monosulfide solution as indicator.

DESCRIPTION OF METHOD

The Fehling solution used is made up as follows:

A. FEHLING'S COPPER SOLUTION[3]—34.639 g. of carefully selected crystals of pure copper sulfate dissolved in water and diluted to exactly 500 cc.

B. FEHLING'S ALKALINE TARTRATE SOLUTION—173 g. of Rochelle salts and 50 g. of sodium hydroxide are dissolved in water and diluted to exactly 500 cc. The solution of sodium monosulfide is made up by dissolving 4 g. of crystalline sodium monosulfide in 100 cc. of water. It should be made fresh every day. The test is conducted in a test tube $8^1/_2 \times {}^3/_4$ in. A wooden clamp for holding this tube should be provided. A spot tile with six or more cavities, a 10 cc. pipette, some straight pipettes, and a burette for the sugar solution completes the outfit.

To make a determination, 10 cc. of the mixed Fehling solution are pipetted into the test tube. The sugar solution, which should contain between 200 and 400 mg. of dextrose or an amount of other sugar equivalent in reducing value to these amounts, is then run in, starting with 8.5 cc. The solution is then boiled one minute, counting from the time a bubble of steam first traverses the entire length of liquid. After the addition of 8.5 cc. and boiling, the color is noted. If the solution is very blue, the sugar solution may be added 2 cc. at a time, boiling 15 seconds after each addition. When the solution in the tube is only a faint blue, a drop of it is added to two drops of sulfide solution on the tile. The tile is given a slight rotary shake and the color of the spot noted. It will be seen that the suspended cuprous oxide turns black and settles at once, while the supernatant liquid turns a more or less intense yellow. The sugar solution is now added to the test tube in smaller portions, depending on the intensity of the yellow coloration, boiling 15 seconds after each addition. It is usual in this laboratory to use 0.4 cc. at this point. As the color becomes fainter, less is added each time, until finally successive additions are only 0.1 cc. each. As soon as no color is perceived immediately upon the settling of the cuprous compound, the result is read from the burette and the mean of this reading and the previous one taken as the number of cubic centimeters required to reduce the ten cc. taken. The experiment is then repeated, adding enough water to make the final volume up to 30 cc., and 97 to 98 per cent of the sugar solution required in the previous trial. This is then boiled $1^1/_2$ minutes and the exact amount adjusted, which can usually be done in two additions. This final determination should require from four to six minutes from the time the solutions are mixed until the estimation is finished. It will rarely be found that these two determinations differ more than 1 per cent in value from each other. The second determination is the one to be used.

When the approximate amount of sugar is known, as it is in most cases, the first approximation can be made much closer and the two titrations given equal weight.

NOTES ON THE METHOD

The time of boiling after $^1/_2$ minute seems to play a comparatively unimportant part. In a series of experiments 99 per cent of the sugar (dextrose) required to reduce a solution was added and the mixture boiled different lengths of time. The amount required for complete reduction was the same whether the first portion was boiled $^1/_2$ minute or $1^1/_2$ minutes. Too protracted boiling, however, is undesirable on account of evaporation and exposure to air. Hence the total time of boiling should be kept within $1^3/_4$ to $2^1/_4$ minutes.

The desirability of a constant volume in the gravimetric method during the reduction is well known; preliminary experiments showed this plainly. Under the conditions of this method 10 cc. of Fehling solution with a final volume of 50 cc. required as a mean of several determinations 49.3 mg. of dextrose for reduction; 10 cc. with a final volume of 30 cc. required 47.6 mg. for reduction. By making a preliminary titration, bringing the volume up to a constant amount, and adding most of the sugar at once, its reducing values become constant. Even if the reducing values of the 2 or 3 per cent subsequently added vary 20 per cent, the results are still within the limits of the method. As can be seen from the difference shown above, a variation of 2 or 3 cc. in the final volume may be con-

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[1] *J. A. C. S.*, **34**, 928.

[2] *Ibid.*, **38**, 663.

[3] Leach, "Food Inspection and Analysis," p. 591.

sidered negligible. The final volume was arbitrarily selected, as it was the greatest volume at which 0.1 cc. of 0.2 per cent dextrose solution would make a distinct change in color.

A test tube of the size given prevents much exposure to the air, and its liability to boil over when heated too rapidly, prevents excessive evaporation.

Numerous trials were at first made with ferrous sulfocyanide[1] and iodide starch mixture,[2] but it was found that both have a common defect; namely, they become colored on exposure to air without addition of Fehling solution. Attempts to obviate this destroy their sensibility to a large extent. The writer had used sodium monosulfide for some time for colorimetric copper estimations and was impressed by its sensitiveness. Furthermore, there ought to be no tendency for the reoxidation of the copper on mixing with the indicator, as the medium is a reducing one. After a few minutes a yellow color will appear, owing probably to solution of some of the copper sulfide. The absence of color, however, is permanent for sufficient time for an observation to be made, while when copper is unreduced, the appearance of the color is immediate. After the operator has become familiar with the end point, it can be judged very closely by the appearance immediately on addition of the drop. As long as unreduced copper is present, a yellowish color is perceptible without agitation, while when all the copper is reduced, the only shade is the reddish brown of the cuprous oxide.

Proteins, and metals which give colored sulfides interfere with the end point. For the former, the writer boils a measured volume and adds alumina cream while still hot, then cools and makes up to a convenient volume, adding sufficient water to correct for the volume occupied by the alumina. The solution can then be allowed to settle and the clear supernatant liquid used, or if time is an object, it may be filtered. This method works very well on most urines and colored solutions. For removing the metals, methods will doubtless suggest themselves.

RESULTS OBTAINED

Various dilutions of a sugar solution were made up and given to a member of the staff (without information as to their sugar content), who obtained the following figures.

No. of cc. used in titration	Mg. total dextrose present
23.30	47.60
15.65	47.75
11.70	47.60
9.35	47.75

It must be understood that this was not pure dextrose, as the purpose was only to see whether results were constant and independent of the concentration of the titrating solution over comparatively wide limits. The above results were each obtained with one titration besides the preliminary one.

Impure maltose solutions were titrated in a similar manner.

No. of cc. used in titration	Mg. total maltose present
23.2	92.8
15.5	93.0
11.6	92.4
9.25	92.5

The following results show the remarkable constancy of results over long periods. The titrations are on 5 cc. of mixed Fehling solution, which was the original manner of using the method, but it was changed to increase the accuracy of the end point.

6/11/1914 5 cc. Fehling reduced by 44.43 mg. crude maltose
8/26/1914 5 cc. Fehling reduced by 44.47 mg. crude maltose

For each value four concentrations were titrated. This constancy is not confined to maltose, but is also true of dextrose. The dextrose factor for 5 cc. in May was 23.6 mg. and in August 23.8 mg.

The writer advises the standardization of the Fehling solution by each user, and hence his factor should not be accepted as final. A mean of four determinations on pure glucose from two different sources in which the maximum variation from the average was ±0.15 mg., gave 47.5 mg. dextrose as the value of 10 cc. of a Fehling solution whose copper content had been accurately adjusted by a sodium thiosulfate solution standardized with pure copper. As can be seen, the factors, once obtained, need be determined only at rare intervals. Pure dextrose, prepared by the Bureau of Standards, is now available for this purpose.

SUMMARY

The writer describes a modification of Fehling's volumetric method designed to do away with some of its sources of error.

The use of a new indicator is described which, so far as is known, is here first used for that purpose.

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[1] Ling Rendle and Jones, Allen's "Commercial Organic Analysis," 4th edition.

[2] F. F. Harrison, Sutton's "Volumetric Analysis," 10th edition.

A COMPARISON OF THE GUNNING-COPPER METHOD WITH THE KJELDAHL-GUNNING-ARNOLD METHOD FOR THE DETERMINATION OF NITROGEN

By Ove F. Jensen

Received June 3, 1914

In 1908 the Association of Official Agricultural Chemists officially adopted[1] a modification of the Gunning method for the determination of nitrogen which prescribes the use of 0.1 to 0.3 g. of crystallized copper sulfate in addition to the potassium sulfate. Penny,[2] in his report on the determination of nitrogen in 1907, says of this modification: "The claims made for the catalytic action of copper sulfate seem to be justified by experience, and there is reason to suppose that this reagent will do much to shorten the time of digestion." Although possessing many advantages over the other methods in use at that time, it was not generally adopted. More recently another modification known as the Kjeldahl-Gunning-Arnold[3] method has been proposed. This method differs from the Gunning-Copper method, only in the use of metallic mercury instead of copper sulfate. In a recent number of This Journal,[4] Trescot shows, very conclusively,

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[1] U. S. Dept. Agr., Bureau of Chemistry, *Bull.* **122**, p. 183.

[2] *Ibid.*, **116**, p. 43.

[3] *Ibid.*, **108**, p. 15.

[4] Vol. **5** (1913), 914.

that the Kjeldahl-Gunning-Arnold method reduces the time of digestion over the original Kjeldahl or Gunning methods from four hours to one and one-half hours. This is a very important item in laboratories where a large number of nitrogen determinations are being made. The Gunning-Copper method has been in use in this laboratory for the past nine years, and the general practice has been to digest from two to three hours after the solution becomes clear.

Since this method possesses several advantages in manipulation over the Kjeldahl-Gunning-Arnold method, a comparison of the two methods with different periods of digestion was undertaken, using bone meal, dried blood, cyanamide, and linseed meal as representative substances. In Table I, the period of digestion in all cases refers to the length of time after the solutions became clear. In the length of time required to become clear, no difference was noted in the two methods. Using a moderate flame, the time required for the sulfuric acid solution to become clear was as follows:

Bone meal...........	25 min.	Cyanamide..........	20 min.
Dried blood..........	25 min.	Linseed meal........	35 min.

TABLE I—EFFECT OF DIFFERENT PERIODS OF DIGESTION ON PERCENTAGES OF NITROGEN FOUND

Period of digestion after solutions became clear	1 hour				1½ hours				2 hours				3 hours			
METHOD	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.
BONE MEAL:																
Gunning-Copper............................	6	2.18	2.16	2.16	4	2.20	2.18	2.19	6	2.20	2.18	2.19	6	2.23	2.20	2.20
Kjeldahl-Gunning-Arnold..................	6	2.25	2.19	2.20	4	2.20	2.18	2.19	6	2.23	2.19	2.20	6	2.22	2.20	2.20
DRIED BLOOD:																
Gunning-Copper............................	6	14.11	14.03	14.07	6	14.24	14.07	14.13	6	14.32	14.15	14.22	6	14.40	14.23	14.29
Kjeldahl-Gunning-Arnold..................	6	14.32	14.11	14.24	6	14.32	14.19	14.29	6	14.30	14.19	14.25	6	14.34	14.15	14.26
CYANAMIDE:																
Gunning-Copper............................	6	15.75	15.37	15.52	6	15.62	15.50	15.53	6	15.67	15.46	15.55	6	15.58	15.50	15.53
Kjeldahl-Gunning-Arnold..................	6	15.62	15.46	15.55	6	15.54	15.41	15.49	5	15.62	15.50	15.55	6	15.62	15.50	15.55
LINSEED MEAL:																
Gunning-Copper............................	6	5.53	5.45	5.49	5	5.62	5.50	5.57	6	5.62	5.50	5.55	6	5.64	5.56	5.62
Kjeldahl-Gunning-Arnold..................	6	5.62	5.53	5.56	4	5.62	5.59	5.61	6	5.59	5.53	5.58	6	5.62	5.56	5.58

The results seem to indicate that a digestion of one and one-half hours is sufficient to produce a quantitative yield of ammonia in either method, except in the dried blood, where from two to three hours are necessary in the Gunning-Copper method. Hibbard[1] found three hours to be necessary, using this method. On the whole, the results are slightly in favor of the Kjeldahl-Gunning-Arnold method, as a quantitative yield of ammonia is produced after a digestion of from one to one and one-half hours. However, it is doubtful if there are many substances for which the Gunning-Copper method will not give an equally high yield with the same length of digestion. In order to test this point, determinations were made on a number of substances such as are encountered in a fertilizer or food laboratory. Three determinations were made on each substance by each method. The data are given in Table II.

TABLE II—DETERMINATIONS OF NITROGEN ON VARIOUS SUBSTANCES

METHOD	Gunning-Copper			Kjeldahl-Gunning-Arnold		
Period of digestion	1½ hours			1½ hours		
SUBSTANCE	Max.	Min.	Av.	Max.	Min.	Av.
Gelatin................	15.14	15.12	15.13	15.16	15.04	15.09
Egg albumin (dried)....	12.86	12.75	12.80	12.86	12.80	12.83
Peptone................	14.49	14.38	14.45	14.49	14.38	14.43
Casein.................	13.87	13.81	13.83	13.92	13.81	13.85
Feathers...............	14.49	14.43	14.47	14.54	14.38	14.46
Leather................	4.83	4.72	4.76	4.80	4.75	4.78
Fish scrap.............	6.48	6.35	6.43	6.51	6.43	6.47
Animal tankage........	6.32	6.26	6.31	6.35	6.29	6.33
Garbage tankage.......	2.99	2.96	2.98	3.00	2.96	2.99
Beef scraps............	9.14	8.97	9.04	9.05	8.97	8.99
Castor bean pomace....	4.66	4.55	4.59	4.55	4.52	4.53
Cocoa..................	4.01	3.94	3.97	3.97	3.90	3.93
Cottonseed meal.......	7.33	7.30	7.31	7.29	7.24	7.26
Cottonseed meal.......	6.43	6.40	6.42	6.37	6.32	6.35
Silage (dried).........	1.30	1.26	1.28	1.29	1.26	1.27
Flour..................	2.43	2.41	2.42	2.44	2.43	2.43
Bran...................	2.60	2.55	2.58	2.58	2.58	2.58
Bone meal..............	3.06	3.02	3.04	3.11	3.02	3.07
Peat...................	2.41	2.37	2.38	2.37	2.36	2.37

The results obtained for these substances by the two methods show a very close agreement, and in point of accuracy there is no choice between them. The Gunning-Copper method possesses several distinct advantages over the other which may be enumerated as follows:

I—The use of potassium sulfide is unnecessary, and thus one detail of manipulation (addition of K_2S) is eliminated, slightly shortening the time required for the determination. Also the presence of hydrogen sulfide in the laboratory from this source is avoided.

II—In adding the sodium hydroxide before distilling, the copper sulfate acts as an indicator, so that a large excess of alkali is easily avoided, and the bumping during distillation is much lessened.

III—The difference between the price of copper sulfate and metallic mercury, and the elimination of potassium sulfide, makes the Gunning-copper method somewhat cheaper.

SUMMARY

A quantitative yield of ammonia in dried blood is produced sooner in the Kjeldahl-Gunning-Arnold method than in the Gunning-Copper method. In the case of all the other substances studied, a digestion of one and one-half hours proved equally efficacious for either method.

The Gunning-Copper method possesses advantages in manipulation which make it preferable to the Kjeldahl-Gunning-Arnold method, especially where a large number of determinations are to be made.

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COMPARISON OF A FEW METHODS FOR TOTAL PHOSPHORIC ACID IN SUPERPHOSPHATE[1]

By C. A. PETERS

Received October 5, 1914

A comparison of several methods for the determination of total phosphoric acid in superphosphate has been made, emphasizing the interference of silica in the gravimetric method, and showing that shorter methods give as accurate results as the customary double precipitation as phosphomolybdate and ammonium

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[1] THIS JOURNAL, 2, 464.

[1] Taken from a thesis by Arthur G. Weigel, optionally presented for the degree of B.S. at the Massachusetts Agricultural College at Amherst.

magnesium phosphate. Nothing new is claimed for the work.

The superphosphate used was home-made from ground rock. All but about three-quarters of one per cent of the phosphoric acid was water-soluble. Aqua regia was used to dissolve the phosphoric acid.

For the determination of the phosphoric acid various procedures were carried out as follows:

A—The Official Method.[1]

B—The Official Method modified by evaporating the liquid on a water bath, taking up with dilute nitric acid and filtering through paper to remove silica before precipitation.

C—Direct weighing of the yellow precipitate as outlined by Baxter.[2]

D—The volumetric process of Pemberton as described by Wiley.[3]

E—The direct precipitation of ammonium magnesium phosphate in the presence of ammonium citrate.[4]

F—Same as E, substituting citric acid for ammonium citrate.[5]

None of these methods require description. However, the apparatus used for heating the yellow precipitate to 290°–300°, as outlined by Baxter, will be described. This consisted of two 6-in. iron dishes, deep form, such as are used for sand baths. The edges of one dish were cut back $^3/_4$ in. every half inch and bent in so as to make a cover for the uncut dish. A hole in the top of the cover held a cork and thermometer. Triangles inside were arranged to hold two or three crucibles, each covered with a small watch glass. An asbestos jacket consisting of a side and top prevented the radiation of heat. The whole was heated with a Bunsen burner, the flame being protected from draft by an iron conical shield 8 in. high.

The results obtained by the different methods are given in Table I, each determination made being listed.

TABLE I—TOTAL PHOSPHORIC ACID IN SUPERPHOSPHATE

METHOD	DUPLICATES Per cent	Average Per cent	Variation from B Per cent	REMARKS
A—Official Method...	15.30 15.25	15.28	+0.26	No silica removed
B—Official Method (modified).........	15.07 14.97	15.02	0.00	Silica removed
C—Direct weight of yellow ppt.........	14.81 14.81			
	14.82 14.85	14.82	—0.20	Temp. 290°–300°
C_1—Same as C but overheated........	14.53 14.54	14.54	—0.48	Temp. 300°–330°
D—Volumetric method...........	14.80 14.86	14.83	—0.19	KOH : HNO_3
E—Pptd. as NH_4Mg-PO_4..............	14.85 14.94			
	14.85 14.87	14.88	—0.14	In am. citrate
F—Pptd. as NH_4Mg-PO_4..............	16.50 16.29	16.39	+1.37	In citric acid

From the comparison of the results given under A and B in Table I it would be inferred that there was 0.26 per cent of silica in the pyrophosphate when the solution of total phosphoric acid before precipitation with molybdate was not evaporated to dryness. The results indicated under C, D and E, which were obtained by direct weighing of the yellow precipitate by the volumetric method and by precipitation in ammonium citrate, are, on the average, 0.17 per cent less than those listed under B. If the results obtained under B—silica-free—are taken as standard, then it is apparent that either of three more rapid methods (C, D or E) give as accurate results as the Official Gravimetric Method. No attempt was made to find silica in any of the precipitates as its presence is generally acknowledged.[1] The results given under C_1 show the decomposition of ammonium molybdate by temperature over 300° and the resulting negative error.

CONCLUSION

The above work emphasizes what is already known:

I—That the Official Gravimetric Method of determining total phosphoric acid gives high results when phosphoric acid is determined in superphosphate without evaporation of the solution to dryness on a steam bath to remove silica.

II—That several methods other than the Official Gravimetric give equally good results in half the time.

DEPARTMENT OF GENERAL AND AGRICULTURAL CHEMISTRY
MASSACHUSETTS AGRICULTURAL COLLEGE, AMHERST

CLEANING SOILS FOR MICROSCOPIC EXAMINATION

By W. H. FRY AND JOHN A. CULLEN

Received Oct. 22, 1914

In microscopic mineralogical work on soils it is necessary that the grains be transparent or at least strongly translucent and that the grain-surfaces be free from all coatings and adhering material. Where light is not transmitted, the optical properties of the minerals cannot be determined in soil preparations; and where the material carries an appreciable coating of some foreign substance the refractive index determined will be that of the coating instead of the mineral, even though the determination of other optical properties of the grain under examination may remain unaffected.

Many soils have their constituent grains more or less stained and coated by various substances. Often simple washing and drying serve to render them adaptable to microscopic examination. But in a great number of cases the grains are so coated with iron oxides, hydroxides, or both, that other means of cleansing have to be resorted to. That cleansing agent would be most efficient which, while entirely removing the iron and other stains, at the same time had the least decomposing action on the minerals themselves.

Hydrochloric and nitric acids act very energetically upon apatite, the determination of the presence of which is sometimes the primary object of the examination. Sulfuric acid cannot be used for the same reason, and in addition has the disadvantage of decomposing biotite, a common soil constituent.

Several readily available organic acids were tested on various soils, different concentrations of the various acids being used in order to ascertain the most efficient

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[1] *Bull.* **107**, p. 2.

[2] *Am. Chem. J.*, **39** (1902), 298.

[3] Wiley, "Principles and Practice of Agricultural Chemistry," II (1908), p. 160.

[4] Wiley, *Ibid.*, II (1908), p. 88.

[5] Wiley, *Ibid.*, II (1908), p. 98.

[1] Wiley, *loc. cit.*, p. 78.

strength. It has been found that, in general, 10 per cent oxalic acid best serves the purpose. In about 30 minutes it removes the iron stains satisfactorily. Tests upon various soil minerals showed that, with the exception of apatite, it did not affect them appreciably; and in the case of apatite, although there is undoubtedly some effect, it leaves that mineral in a determinable state. Of course, in any case calcite would be removed—a fact which renders very difficult the determination of small quantities of this mineral in discolored soils.

Bureau of Soils
U. S. Department of Agriculture
Washington

LABORATORY AND PLANT

REPORT OF THE SELBY SMELTER COMMISSION

Received December 8, 1914

The filing of the report, findings and recommendations of the Selby Smelter Commission with the Superior Court of Solano County settles finally and conclusively the long continued controversy between the residents of Benicia and the adjacent agricultural country and the Selby Smelting and Lead Company concerning the alleged disagreeable and injurious effects produced by the smoke from the Selby Smelter.

The smelter operated by the Selby Smelting and Lead Company is situated near Vallejo Junction in Contra Costa County, California, at the western end of the Carquinez Straits. The City of Benicia is situated in Solano County at the eastern end of the Straits, about five miles from the smelter. During nine months of the year the prevalent trade winds blow the smoke from the Selby Smelter over and into the City of Benicia and the agricultural area lying between Benicia and Vallejo.

On March 14, 1905, action was brought by the District Attorney of Solano County, California, in the Superior Court of Solano County, praying for an injunction which would restrain and enjoin the Selby Smelting and Lead Company from permitting injurious smoke and gas from the Selby Smelter to blow over and upon the City of Benicia and the tributary country. The case was brought to trial on August 7, 1906, and judgment of the Court in favor of the Plaintiff was rendered on July 16, 1908. The decree of the Court was to the effect that during eight months of each year between the 15th of March and the 15th of November, the Selby Company was enjoined from discharging noxious gases and fumes into the open air in such a manner that the same would be carried into and upon the City of Benicia and the tributary country in Solano County in such quantities as to be offensive to the senses and to interfere with the comfortable enjoyment of life and property.

After motion for a new trial was made by the Defendant and denied by the Court, an appeal was thereupon taken to the Supreme Court of the State. On June 12, 1912, the judgment of the trial court was affirmed by the Supreme Court.

During the period covered by this litigation the Selby Company had been making efforts toward the elimination of some of the objectionable constituents of the smoke, these efforts having resulted in the removal of the major portion of lead, arsenic and sulfur trioxide from the smelter smoke.

In the spring of 1913, although the Selby Company maintained that they had abated the nuisance, complaints were made by the residents of the area that a nuisance still existed, and that the decree of the Court was, therefore, being violated by the Smelting Company.

Various considerations, among them the prospective heavy expense which would accrue to both parties to the litigation as a result of a trial of the Smelter Company for contempt of Court, led to conferences of the attorneys representing both sides, which resulted in an agreement to submit the question of fact as to the violation of the decree of injunction to a board of technically trained men, deemed by both sides to be qualified to act in such a capacity, and equal financial responsibility of the parties in the expense of the Commission's activities. The result of the agreement was the filing of a stipulation in the record of the cause providing for such a board.

ORGANIZATION OF COMMISSION

On May 22, 1913, this board was organized as the Selby Smelter Commission, with the following personnel:

J. A. Holmes, Director U. S. Bureau of Mines.

E. C. Franklin (at the time of appointment Chief of the Chemical Division of the Hygienic Laboratory of the U. S. Public Health Service), Professor of Organic Chemistry, Leland Stanford, Jr., University.

Ralph A. Gould, Chemical Engineer, San Francisco, Secretary of the Commission.

The function of the Selby Smelter Commission was to determine the facts and report its findings on the following:

1—Is the Selby Smelter operating in such a manner as to violate the decree of the Court dated July 16, 1908?

2—If the Defendant Company is violating the decree, what is the extent of the violation?

3—If the Defendant Company is violating the decree, what steps must be taken by the Defendant to avoid a violation of the decree?

For the determination of facts, the Commission and its staff have carried on very careful and complete investigations of all matters which in the opinion of the Commission could have any bearing on the questions at issue and to be answered. These investigations were made by the following staff of trained scientific and technical men, no one of whom, otherwise than in arriving at the truth, was directly or indirectly interested in the findings of the Commission:

A. E. Wells, Metallurgist and Chief Chemist, in charge of Smelter Investigations and Field Work.

C. B. Dutton, Special Legal Agent, U. S. Bureau of Mines.

CHARLES F. SHAW, Professor of Agronomy, College of Agriculture, University of California.

E. E. FREE, Soil Expert and Agronomist.

J. W. BLANKINSHIP, Ph.D., Plant Pathologist.

WYATT W. JONES, Plant Pathologist.

R. W. DOANE, Professor of Entomology, Leland Stanford, Jr., University.

C. M. HARING, D.V.M., Professor Veterinary Science, College of Agriculture, University of California.

K. F. MEYER, D.V.M., Professor Bacteriology and Protozoölogy, University of California.

Through the courtesy of Dean Thomas Forsyth Hunt, of the College of Agriculture, and Professor F. T. Gay, of the Department of Pathology, the Commission had the valued coöperation of several of the staff of the University of California. The facilities of the U. S. Bureau of Mines also were placed at the disposal of the Commission and much assistance was rendered by its staff of experts, especially by Dr. F. C. Cottrell and Dr. L. H. Duschak.

The results of the investigations of the several experts were presented to the Commission in the form of reports, as given below:

1—A Detailed Study of Statements of Residents of the Selby "Smoke Zone" as regards the Presence of a Nuisance in the Area, by C. B. Dutton.

2—Conditions in and around the Selby Smelter and the Selby "Smoke Zone," by A. E. Wells.

3—Investigations to Determine the Extent of the Contamination of the Atmosphere in the Selby "Smoke Zone" by the Smelter Emanations, by A. E. Wells.

4—Investigations to Determine the Sulfur Dioxide Present in the Atmosphere in Places Outside the Selby "Smoke Zone," by A. E. Wells.

5—Conditions of Plant Life in the Selby "Smoke Zone," by J. W. Blankinship.

6—The Occurrence of Sulfur Dioxide Injury to Plants in the Selby "Smoke Zone," by Wyatt W. Jones.

7—Insect Pests in the Selby "Smoke Zone," by R. W. Doane.

8—Agronomic and Soil Conditions in the Selby "Smoke Zone," by Charles F. Shaw.

9—Investigations of Live Stock Conditions and Losses in the Selby "Smoke Zone," by C. M. Haring and K. F. Meyer.

10—Fumigation Experiments to Determine the Effect of Highly Diluted Sulfur Dioxide upon a Growing Grain Crop, by A. E. Wells.

11—Investigations to Determine the Effects of Sulfur Dioxide on Man, by A. E. Wells.

12—The Possibility of Reducing the Sulfur Dioxide Output from the Selby Smelter, by A. E. Wells.

(*a*)—Investigations on the Gases from the Dwight and Lloyd Sintering Machines of the Selby Smelter.

(*b*)—Studies in the Commercial Utilization of the Sulfur Dioxide Produced by the Selby Smelter.

13—Bibliography: The Effect of Sulfur Dioxide on Vegetation and Animal Life, The Chemists' Club Library, New York.

The field investigations upon which these reports are based were conducted between June, 1913, and September, 1914.

In collecting the data for his report, Mr. Dutton interviewed the residents of the "Smoke Zone" in as thorough and as representative a manner as possible, and sought to obtain directly their ideas concerning the existence of a nuisance. The opinion expressed as to the existence of the nuisance and injury from the smelter smoke varied from the extreme of unreasoning radicalism to entire indifference.

A study of Mr. Dutton's report reveals the fact that two classes of odors have been described by the residents of the "Smoke Zone" as "smelter smoke;" one is undoubtedly that due to sulfur dioxide, and the other is that of certain products from the refining of petroleum, the so-called "oil smell." Judging from the statements of these residents, there can be no doubt that in the past, up until 1910 or 1911, there were present at times in the "Smoke Zone" fumes and gases possessing very disagreeable odors, the "oil smell," which could not possibly have been due to smelter emanations. Subsequent to 1911, "oil fumes" have not been so prevalent, but occasionally the odor of sulfur dioxide has been detected.

The conclusions derived from Mr. Dutton's report are that among the greater proportion of the residents there is at the present time only slight, if any, legitimate objection to the presence of "smelter smoke" in the atmosphere of the "Smoke Zone." Under extremely unfavorable conditions and to supersensitive persons, "smelter smoke" may occasionally be smelled in the area, but to the fair-minded person such occurrences do not prevent the enjoyment of life nor are they detrimental to the health of the community.

The Commission considers that one of the most important phases of its investigations has been the direct determination by chemical analyses of the sulfur dioxide contained in the atmosphere of the "Smoke Zone."

This work was conducted under the superintendence of Mr. A. E. Wells, the Metallurgist and Chief Chemist of the Commission, with the assistance of eight trained chemists and six helpers, and is believed by the Commission to be the most extensive and exhaustive of its kind heretofore.

SULFUR DIOXIDE DETERMINATIONS

For the determination of sulfur dioxide, a method has been developed which is believed to be by far the best yet used in work of this character, in that it combines in a most satisfactory manner those characteristics which permit "instantaneous sampling," rapidity of execution, easy field manipulation, and a high degree of accuracy. Concentrations of sulfur dioxide as low as 0.2 part per million of air are rapidly and easily determined by the method as developed and finally adopted by the Commission. For the essential features of the method, the Commission is indebted to Mr. J. R. Marsden, Chief Chemist of the Selby Smelter.

For making observations in the field, two permanent laboratories were established, where sulfur dioxide determinations were made at brief intervals daily, and an automobile was equipped as a portable laboratory, by means of which determinations were made in all parts of the Selby "Smoke Zone," as well as in many places outside the Selby "Smoke Zone."

The field investigations to determine the sulfur dioxide content of the atmosphere in the Selby "Smoke Zone" extended from September 17 to December

15, 1913, and from March 1 to April 15, 1914, during which time 4862 determinations were made. During the same period about 700 determinations were made in places outside the Selby "Smoke Zone."

During the entire course of the investigations, special attention was given to the metallurgical processes going on at the smelter and the amount of sulfur dioxide eliminated from the smelter during the tests in the "Smoke Zone" has been checked by the staff of the Commission. Determinations were made when the wind conditions were the worst possible for the area, and when, at the request of the Commission and under its supervision, the output of sulfur dioxide from the smelter was the highest possible. Other tests have been made with the smelter entirely closed down and with the wind conditions favorable and unfavorable to the "Smoke Zone." Every attempt has been made to obtain these data under all possible conditions, in order that maximum, average and minimum figure might be obtained as to the sulfur dioxide content of the atmosphere of the "Smoke Zone."

Of the total number of "instantaneous" samples (4862) taken in the Selby "Smoke Zone" during the period of field work, 75 per cent contained less than 0.2 part SO_2 per million of air; 86 per cent contained less than 0.4 part SO_2 per million; and over 97 per cent contained less than 1.0 part SO_2 per million parts of air. Only 21 samples, or 0.43 per cent of the total, contained more than 2.0 parts SO_2, and no sample analyzed more than 7.1 parts SO_2 per million.

The higher concentrations were found only when puffs of the smoke from the Selby Smelter were drifted by a gentle breeze over the most exposed portions of the "Smoke Zone," and at no time did a concentration greater than 2.0 parts SO_2 per million persist for a continuous period of more than thirty minutes. The total time during the whole period of the Commission's investigation that the concentration of sulfur dioxide was more than 2.0 parts per million at any part of the "Smoke Zone" was 220 minutes, or 3 hours and 40 minutes.

Only on six occasions was the concentration above 3.0 parts SO_2 per million, and the total time that the concentration was above that amount was 65 minutes. Within the city limits of Benicia itself, the maximum concentration of sulfur dioxide found was 2.4 parts per million, and only 21 out of the 2840 samples taken in this portion of the "Smoke Zone" contained more than 1.0 part SO_2 per million.

In the business section of San Francisco during calm mornings, the concentration of sulfur dioxide was found to be as high as 1.8 parts SO_2 per million. Under brisk wind conditions such as are prevalent during the late morning and early afternoon during the period of trade winds, the sulfur dioxide content was seldom over 0.2 part SO_2 per million. On the Ocean Beach no determinable quantity of sulfur dioxide was found. In Oakland and Berkeley, of the 148 determinations made, none showed a concentration of sulfur dioxide higher than 1.0 part per million. One hundred and three determinations were also made in the vicinity of Richmond, which showed an average value of 1.1 parts SO_2 per million, and a maximum content of 4.5 parts SO_2 per million. In Martinez and vicinity, 168 determinations were made. The average of these determinations was 0.23 part SO_2 per million, and the maximum 1.7 parts SO_2 per million.

The results of these investigations show that, on the one hand, although the atmosphere of other areas investigated show a higher constant concentration of sulfur dioxide than the Selby "Smoke Zone," the maximum concentrations in the Selby "Smoke Zone," on the other hand, are higher than those of any of the other areas investigated. These higher concentrations, however, never persist for more than a few minutes.

SENSITIVENESS OF HUMAN BEINGS TO SULFUR DIOXIDE

In order to determine whether the concentration of sulfur dioxide found in the "Smoke Zone" could be considered sufficient cause for a nuisance complaint, or could be injurious to the health of people residing in the Zone, it became necessary to study the effects of high dilutions of sulfur dioxide upon man and to determine the sensitiveness of various persons to the gas. The following is a brief summary of the results of these investigations:

Of the 60 subjects experimented upon, 32 of whom were previously acquainted with the gas, no one was able to detect the presence of 1.0 part SO_2 per million of air. With concentrations of 2.0 parts SO_2 per million several of the subjects detected the presence of something foreign in the air, but could not identify it, and 2 identified the gas by taste. With concentrations of 3.0 parts SO_2 per million, the greater proportion of the subjects acquainted with the gas were able to identify it, and at 4.0 parts practically all were able to do so. The greater proportion of the subjects not previously acquainted with sulfur dioxide did not identify the gas until the concentration was greater than 4.0 parts per million.

In the investigations to determine what concentration of sulfur dioxide would be considered a nuisance to all persons, very little agreement was found between the ideas expressed as to what was a nuisance. As a general statement, it may be said that concentrations of 3.0, 4.0 and even 5.0 parts SO_2 per million were not considered to be a nuisance even if continued for considerable periods of time; concentrations of from 5.0 to 10.0 parts SO_2 per million if continued for 10 to 15 minutes would be considered a nuisance; concentrations above 10.0 parts SO_2 per million if existing for only a few minutes would certainly be called a nuisance. It was definitely determined that concentrations below that at which the sulfur dioxide can be smelled, that is, below about 3.0 parts SO_2 per million, cannot possibly be considered a nuisance or cause for discomfort.

It will be recalled that in the atmosphere of the city of Benicia the sulfur dioxide concentration never reached 2.5 parts per million during the whole period of the Commission's investigations, and that at one of the most exposed spots in the "Smoke Zone" there were but six short periods when it was above 3 parts, reaching a maximum of 7 parts on one occasion only.

In view of the established facts therefore, it is quite impossible to maintain that during the period of investigations by the Commission the residents of the City of Benicia or of any other part of the "Smoke Zone" have been subjected to a nuisance as the result of discharge of sulfur dioxide from the Selby Smelter.

EFFECT OF SULFUR DIOXIDE ON VEGETATION

Extended experiments were conducted to determine whether such concentrations of sulfur dioxide as are found in the Selby "Smoke Zone" are capable of doing any injury to crops or other vegetation growing in the Zone.

The plan of these experiments was to allow barley plants to grow normally in an open field, and occasionally and for definite periods of time to subject the plants to definite concentrations of sulfur dioxide. These experiments were carried out with the following object in mind:

1—To determine the visible injury produced by definite concentrations of sulfur dioxide applied for definite periods of time.

2—To determine the economic injury or decrease in yield resulting from the visible injury produced.

3—To determine the possibility of "invisible injury" to a growing grain crop and the extent to which this may take place.

In a field of growing barley, experimental plots four feet by twenty feet in area were laid out, and covered during periods of fumigation with a cabinet designed so as to interfere as little as possible with the illumination of the plot. The sulfur-dioxide-air-mixture was blown in at one end and allowed to escape at the other, in such a way as to maintain a steady stream of air containing sulfur dioxide through the cabinet during the fumigation periods. The length of time of each fumigation varied between two minutes and one hour.

Experiments were carried on simultaneously on a farm near Vallejo and at the University farm at Davis. At Vallejo, 106 plots, and at Davis 35 plots were experimented upon, with results which were concordant in every respect.

A concentration of 5.0 parts sulfur dioxide applied for an hour under ordinary humidity conditions produced considerable visible injury. Visible injury is produced on growing barley by concentrations of 1.0 part SO_2 per million of air if the length of time of application is sufficiently great. Thus, 3 fumigations of 7 hrs. each produced slight visible injury and no reduction in yield, with air containing 1.0 part sulfur dioxide per million. Sixty-two fumigations of one hour each, with 0.5 part SO_2 per million, irregularly continued through the growing period, produced very slight visible injury and no reduction in yield.

From a study of the results of these experiments in connection with the information gained from the investigations upon the sulfur dioxide content of the atmosphere of the "Smoke Zone," the Commission has found that from time to time conditions may arise under which slight visible injury will be visited upon susceptible plants growing on the more exposed portions of the "Smoke Zone." Since, however, plants will endure a considerable amount of visible injury without any diminution of crop yield, the Commission concludes that within the "Smoke Zone" no economic damage results from the smoke of the Selby Smelter. This conclusion receives convincing confirmation from the observations of the Commission's plant pathologists, who have found no indications whatever of economic sulfur dioxide damage within the area of the "Smoke Zone." It was found that when the plants were at one time badly bleached this fact did not necessarily mean a decrease in the yield. A number of plots badly bleached in the early stages of growth were observed to recover rapidly, and it was found that their yield at maturity averaged within three per cent of the yield from the check plots. Short time fumigations repeated a great many times, and of sufficient intensity to keep the foliage bleached throughout the season, were much more effective in reducing the yield than were one or two very strong fumigations.

No economic damage or loss as expressed in decreased yield of crops or decrease in the fertility of the seed resulted from the treatment of barley plants with quantities of sulfur dioxide insufficient to produce marked visible injury. Thus, there was no indication of an economic "invisible injury."

AGRICULTURAL CONDITIONS IN "SMOKE ZONE"

For the determination of the condition existing in the "Smoke Zone" as regards the crops of various kinds and the many kinds of plant life found therein the Commission engaged two plant pathologists of a high degree of training and of extensive experience in the study of plants in relation to smelter smoke injury. Each was commissioned to make a complete plant pathological survey of the area, reporting all abnormal conditions which exist and to trace, wherever possible, the actual cause of such conditions. The only conclusions which can be drawn from the work done in the plant pathological survey are that such poor conditions of plant growth as exist in the "Smoke Zone" are directly traceable to one or more of the following causes: plant diseases, predacious insects, poor soil, poor cultivation, lack of water and indifference to all of those conditions by the farmers of the area. None of the conditions existing so far as vegetation is concerned can be attributed to the effects of the smoke from the Selby Smelter.

From a consideration of the data collected during the entomological survey, the general conclusion reached is that lack of cultivation, lack of proper pruning, absence of spraying and fumigation with insecticides are mainly responsible for the unusually bad condition which exists among the trees, vines and shrubs in the Selby "Smoke Zone." The indifference of certain farmers to these conditions is illustrated by the fact that, during his investigations, Professor Doane volunteered to advise the farmers free of charge as to the proper methods for combating insects and to supervise their attempts, yet none of them accepted his services or took advantage of the opportunity to improve existing conditions.

SOIL INVESTIGATIONS

The problems presented to the agronomic soil experts were:

1—Are the agronomic conditions of the "Smoke Zone" such as to conduce to high agricultural development?

2—Does there exist in the "Smoke Zone" any soil trouble which is responsible for any poor condition of plant growth which may exist?

3—Has the soil of the "Smoke Zone" been polluted by materials deposited therein from smelter smoke?

4—If such pollution exists, is it of economic importance? May it influence the growth of crops or plants for good or for ill?

The yield of crops in the area are below the average for areas in other sections of the state having the same climate. The poor quality of the soil and the poor agricultural practices are sufficient to account for the existing bad conditions as to crops and crop yields. No soil trouble exists, other than the poor quality of the soil, to which the existing conditions of plant growth can be traced.

In the matter of soil pollution, an extensive investigation was conducted. Samples of soil were taken from various portions of the area and subjected to examination to determine the presence of lead and arsenic. These metals were found to be natural constituents of the soils of the "Smoke Zone" and the country surrounding the "Smoke Zone." A slight increase in the lead and arsenic present in the soil was found in the area nearest the smelter, but this increase was shown to be of no economic importance.

Supplementing this work, the data collected by Mr. Wells on the presence of lead and arsenic in the air before the installation of the roaster baghouse proved that although lead and arsenic were present, the amount was unimportant from the point of view of soil contamination.

EFFECT OF SMELTER FUMES ON HORSES

The veterinary survey included the identification of every horse and the enumeration of all the other important domestic animals within the Zone. The listing of the horses developed the fact that 31 horses out of a total of 308 within the "Smoke Zone" were suspected as being of the type known as "roarers;" 12 of these 31 were diagnosed as "roarers," the "roaring" condition being brought about directly by the paralysis, either partial or complete, of certain muscles of the throat and neck, which causes improper functioning of the respiratory system, so that under exercise the animal so affected breathes with a peculiar roaring sound.

It was the opinion of the experts that the condition of these roarers was due to chronic lead poisoning and that the animals had been injured by smelter smoke.

INSTALLATION OF BAGHOUSE FOR ELIMINATION OF VISIBLE SMOKE

Soon after beginning its investigations, the Commission came to the conclusion that a study of the atmosphere of the "Smoke Zone" uncontaminated by the visible element of the smoke of the Selby Smelter would be highly desirable. The Selby Smelting and Lead Co. were, thereupon, requested by the Commission to take steps to remove all solids from the smoke that was being discharged from the plant. The Selby Company, with commendable promptness, began the erection of a baghouse, by means of which the visible smoke from the roaster stack (the only source of visible smoke) could be eliminated. The Commission's request was made October 25, 1913, and the installation of the baghouse was completed April 1, 1914, at an expense to the Selby Smelting and Lead Co. of approximately $35,000.

In order that full information might be at hand upon which to base recommendations for the subsequent operation of the smelter, in the event that a nuisance was found to exist within the "Smoke Zone," the Commission early undertook certain studies to determine the possibility of eliminating the sulfur dioxide from the smoke of the plant before the latter is sent into the atmosphere.

An investigation was conducted to determine the possibility of operating the Dwight and Lloyd Sintering machines of the plant in such a manner as would allow the production of a gas with a sulfur dioxide content sufficiently high for its recovery as a by-product. As a result of this investigation, it was found that by a proper preparation of the charge and the recirculation of a part of the gases, that 80 per cent of the total sulfur dioxide eliminated by the machines can be concentrated in a volume containing 7.5 per cent sulfur dioxide. With this concentration it is possible to apply a commercial scheme for recovery by the production of sulfuric acid, liquid sulfur dioxide or sulfur.

FINDINGS OF COMMISSION

From the personal investigations by the Commission and from a study of the various reports presented, the Commission finds that:

I—The Smelter Company violated the injunction up to April, 1914, with respect to damage to certain horses in the "Smoke Zone," and that this violation ceased when the roaster stack baghouse was installed.

II—The Smelter Company has not violated the injunction with respect to disagreeable odor maintained in the "Smoke Zone," nor with respect to injury produced on crops or vegetation or on domestic animals through emitting sulfur dioxide into the atmosphere.

III—The Smelter Company will not violate the injunction if it discharges less than 80 tons of sulfur dioxide per 24 hours into the atmosphere, and cleans the smoke of its visible element.

IV—The Smelter Company will not violate the injunction, if for purposes of cleaning or repairing the baghouse, visible smoke is discharged for periods not to exceed a total of 48 hours in any one month.

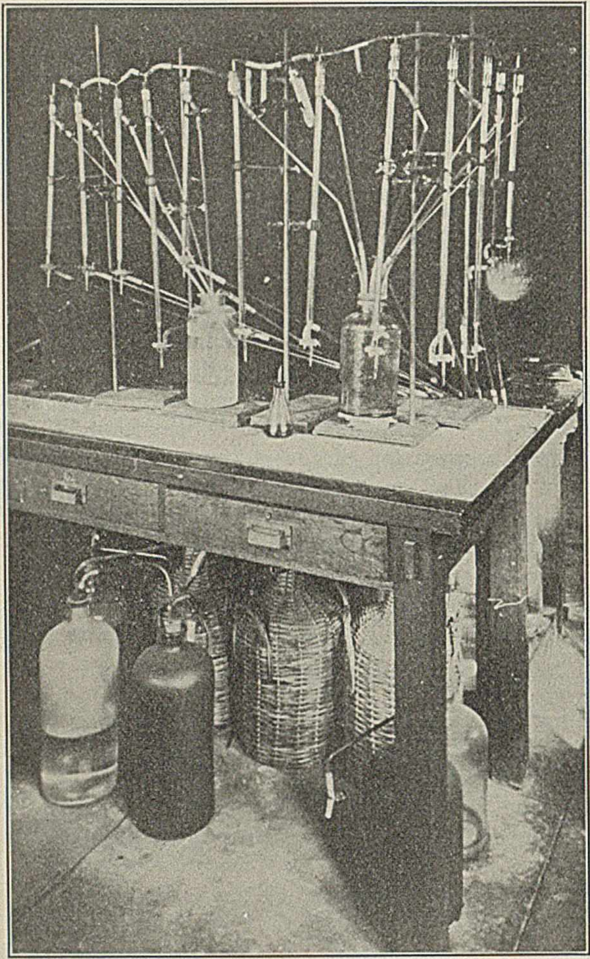
Selby Smelter Commission
325 Monadnock Building, San Francisco

A TITRATION TABLE

By R. S. Potter and R. S. Snyder

Received October 17, 1914

In the course of some work which was being carried on here at one time, twelve different standard solutions were required and a space-saving disposition of these was necessary. The arrangement which has been found very practicable is shown in the accompanying illustration. Others might find something similar of some use, so a brief description of the apparatus shown will be given.



TITRATION TABLE

From the large bottles which are kept on the floor under the table and which contain the various solutions, delivery tubes run up through suitable holes in the back of the table to their respective burettes. The burettes used are of the three-way stopcock, overflow, zero point type. Tubes from the overflows of the six burettes at the right, which do not need to be protected from the air, lead to the large waste bottle at the right as shown. Entering this bottle is a tube connected to an ordinary air pump. The disposition of the burettes which are used for solutions to be protected from carbon dioxide is somewhat different. The tubes from the overflows lead to the large, open waste jar as shown. At the rubber connection of each of these overflows is a pinch-cock, which is kept closed, except as will be pointed out below. The upper openings of all the burettes are connected as shown, and a soda lime tube placed next the first burette, whose solution is to be protected from carbon dioxide. An open T tube is placed in the series of connections as shown.

The operation of the apparatus is as follows: The pump is turned on; the open end of the glass T is closed with the finger and if it is desired to use one of the six solutions to the right, the respective stopcock in the burette is opened; the solution is drawn up and the excess runs into the waste jar. If a solution which is to be protected from the carbon dioxide is to be used, the operation is just the same, except that any excess solution in the overflow cup must be gotten rid of by opening the corresponding pinch-cock in the overflow tube. Siphon tubes are kept in the two waste jars to draw off the waste solutions as they accumulate. As the rapidity with which the solutions are drawn up depends upon the rapidity with which a partial vacuum is created, it is better either to have the waste jar to the right small, or as we have done, keep a large one nearly full of water. It is scarcely necessary to state that all the overflow tubes might have been connected to the one bottle shown at the right, but space in the rubber stopper prohibited. The apparatus here shown was set up eight months ago and no changes nor repairs have been necessary during that time.

This scheme has the following advantages:

I—The minimum table space is taken up.

II—The solutions left in the burettes and delivery tubes can be automatically returned to the respective stock bottles whenever that is desirable.

III—A leak will not cause a loss of solution and a sometimes disastrous flood, as is the case when the stock solution is kept on a shelf above the burette.

SOIL CHEMISTRY LABORATORY
STATE COLLEGE EXPERIMENT STATION
AMES, IOWA

A BLAST LAMP FOR NATURAL GAS

By HAROLD CANNING CHAPIN

Received December 7, 1914

The simple arrangements here illustrated, having served this laboratory for a year, may be of interest to others using natural gas. For complete combustion methane requires four times as much oxygen as does either hydrogen or carbon monoxide. Hence natural gas, which averages over 90 per cent methane and related hydrocarbons, will not burn completely in the amount of air which suffices for an equal volume of coal or water gas. Adjustment of a coal gas burner for natural gas requires cutting down of the gas-air ratio, which unfortunately is opposed by the higher pressure at which natural gas is usually supplied.

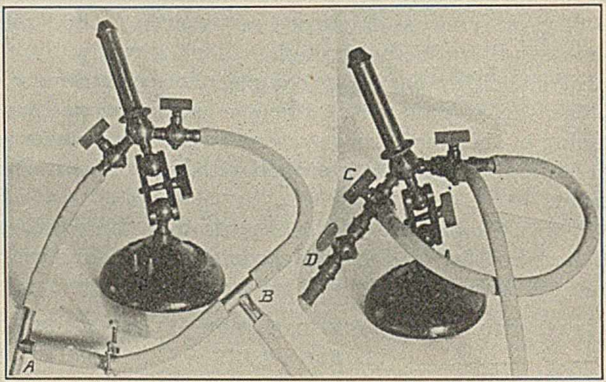


FIG. I FIG. II

The best flame obtainable with a blast lamp in the ordinary way is not very hot and smells of escaping gas, which is not only disagreeable but also likely to have a reducing action on platinum. Except with small flames it is impossible to mix sufficient air with the gas in the regular place at the tip of the burner without using so large an excess that the flame necks down and blows out. Mixing can be effected by placing a burner an inch or so from the lamp tip. The flame then starts mainly from the auxiliary burner, allowing the required air to be sucked into the intervening space. This serves for heating dishes, etc., but the flame is noisy and too poorly defined for glass-blowing.

Improvement was effected by admitting air to the gas current at a point back of the burner, as shown in Fig. I. Part of the air is diverted at A and mixed with gas at B. It proved essential at the pressures used, that the air follow the straight course at B with the gas entering at right angles. Fig. II shows the same arrangement incorporated in the lamp by shifting of parts and addition of a few stock fittings. Cock C replaces the pinchcock of Fig. I. D is a three-way cock made by drilling an open two-way cock from surface to center of stopper and cutting away from the stopper the partition between the new hole and half the old one. This was added to permit escape of air cut off from the lamp, thus allowing better regulation and relieving rubber connections from the high pressure of our laboratory air pipes. For small flames the cross connection can be closed; for larger it can be opened until the flame reaches the desired diameter next the burner tip. In this way, with air at 20 lbs. per sq. in. and natural gas equivalent to 20 in. of water, there can be maintained quiet flames with sharp 3 in. inner cones or good diffuse flames of larger dimensions.

Research Laboratory, National Carbon Company
Cleveland, Ohio

ADDRESSES

THE HARDWOOD DISTILLATION INDUSTRY IN AMERICA[1]

By Edward H. French and James R. Withrow

In view of the economic importance of the utilization of wood waste, and the increasing interest manifested in this utilization, it naturally surprises the inquirer that there is practically no literature upon this industry from the point of view of actual American practice. It may not be without value, therefore, to consider the progress made in hardwood distillation, and to trace its development from its inception in this country. We have gathered together consequently and classified much of the information which we have acquired in the plants of this industry during an experience in it totaling about 25 years.

This tracing of the development of an industry of the magnitude of this one is peculiarly interesting to the engineer, since it shows the necessarily slow evolution of the industry in the hands of the unscientific manipulator, and serves not only to emphasize the advantages possessed by the modern chemical engineer, but also to indicate how much more rapid the development might have been in the hands of experienced chemical engineers. It indicates also that in the future, under the direction of the competent engineer, important advances may be made much more rapidly than in the past. This latter statement is significant when it is remembered that progress thus far has been due either to accident or very often to workmen endeavoring to minimize the laboriousness of their work. As plants are operated in 12-hour shifts, this desire to economize energy may be readily understood.

For much of the historical information collected we desire to express our appreciation to Mr. Robert Mackay, who has been active in this industry for so many years. In fact during the past fifteen years our own continued intimate acquaintance with Mr. Mackay has been not only of unusual pleasure but of continuous instruction. A history of this industry would be incomplete without mention of the fact that, due largely to his personality and integrity, the firm with which Mr. Mackay is identified has had the unusual experience, in an extensive industry, of supplying engineering materials for every plant of this nature in the United States and Canada with perhaps two exceptions, for a period covering the past 25 years.

EARLY HISTORY

While charcoal burning was doubtless carried on in the earliest days in this country, it was not until 1830 that James Ward[1] began the manufacture of pyroligneous acid, at North Adams, Mass. No claim is made that the pyroligneous acid was carried further though it may have been. We have, ourselves, no information on this matter other than the above citation. As far as we can ascertain, it was not until 1852 that works in the modern sense were inaugurated for the distillation of wood for the production of volatile products, and their semi-refined products. This does not appear in agreement with W. L. Rowland,[2] who is later cited by Monroe and Chatard and C. L. Campbell,[3] all of whom state that the manufacture of acetate of lime and methyl alcohol was started in the United States about 1867 by James A. Emmons and A. S. Saxon, in Crawford Co., Pa. Our information in this case comes from various manufacturers who have been in this business from the earliest times or at least whose family connections with it go back to the beginning. One of these sources is Mr. Neil Patterson, whose father was in charge of the original "Scotch Works," built in 1852.[4] In this year the Turnbull Company, of Glasgow, Scotland, who were engaged there in the copper and iron industry as well as that of wood distillation, built the first operation in this country, by way of expanding their "old country" business. The place chosen for this location was known as Millburn, New York, now Conklin's Station, on the D. L. and W. R. R., not far from Binghampton.

The Turnbull Company brought with them their apparatus as well as men experienced with their methods. On account of these Scotch workmen the works became known as the "Scotch Works," and this name has clung to it to the present time, although the original workmen gradually went with new operations which started shortly after this one. They had much to do with the subsequent expansion of the industry, all of them being later in charge of new works.

It is interesting to note in connection with this first plant, that it was a type that was copied in detail in the construction of those that followed, for many years afterward. All these plants were equipped with cast-iron cylinders 42 in. in diameter and 9 ft. long, set in pairs; thus each pair held about $1^1/_4$ cords of wood. The wood was cut 7 ft. long and the charge "run

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[1] Read before the 7th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 4, 1914.

[1] Monroe and Chatard, "Chemicals and Allied Products," 12th Census, United States, *Bull.* **210**, 34.

[2] Special agent 10th U. S. Census on Chemical Products and Salt, p. 23.

[3] *Met. and Chem. Eng.*, **1910**, p. 155.

[4] Mr. J. L. Stuart of Corbett and Stuart, one of the earliest firms in this business in this country, informs us that the date 1852 given by Mr. Patterson for the building of the Turnbull plant should be 1849.

off" every 12 hours, and 6 days a week. The stills and pans were operated during these early days exclusively by direct firing. The fuel used for the retorts, stills and pans was the charcoal produced, over which was poured the residual tar to make a quick fire.

This original works was followed in 1865 by Emmons & Co., of Brookdale, N. Y. In 1868 Alonzo Smith started a plant at Sturroco, Pa. Keery Brothers, Cadosia; Mandaville, Emmons, Corbett and Mitchell, Livingston Manor, N. Y.; King and Co., Acidalia, N. Y.; Hilton & Co., Hiltonsville, N. Y.; Brand & Schlayer, Frink & Ross, Tyler & Hall, Inderlied & Co., Bayless & Berkalue, and Wright & Co. were also early in the field.

During the early part of this period of development, the chief product desired was acetate of lime, for which from 12 to 15 cents per lb. was obtained. The alcohol demand was almost negligible; that made was of very inferior quality and was kept in barrels, and most of it was lost by evaporation or through some "illegal vent." The charcoal also had but little commercial value and was largely consumed as fuel at the works, although a small local demand gradually developed, starting with the neighboring tinsmith.

The change from the old charcoal heaps or pits to the kilns probably came quite early and perhaps before any of the improvements we have mentioned. It was not until 1876, after the retort system was well established and markets for its products had been developed, however, that Dr. H. N. Pierce's inventions made it possible to utilize partially the products wasted in the smoke from the charcoal kilns in Michigan, where great quantities of charcoal were prepared for blast furnace use.

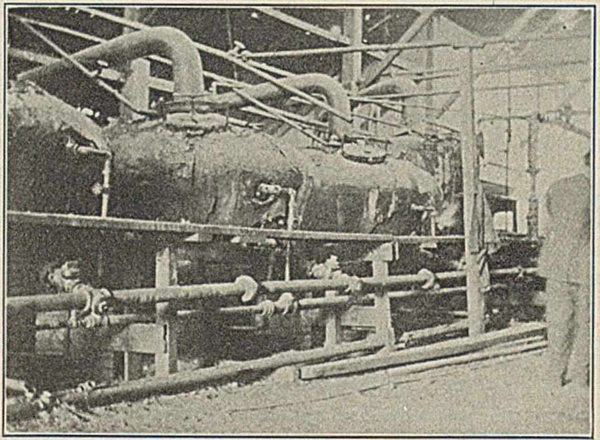
The earliest attempt at refining alcohol, so that it might be of commercial value, was made by a Mr. Pollock, a chemist, living just out of New York City. In a short time a demand began to develop for this product, which steadily increased, and up until 1880 was at all times up to the dollar mark. It was during this period that the need of better refining was felt, as it was realized that a large loss was entailed in the refining operations. This necessity accounts for the coming of the Burcey pans in the early seventies. These are copper containers placed in the vapor line above the stills, with deflectors inside to project the vapor against the upper shell of the container, upon which a stream of water runs, causing fractional separation of the water from the alcohol vapor. The increase of alcohol product resulting from this improvement, together with the increasing market demand, made a central refinery necessary, and the producers united in building a refinery at Binghampton, N. Y., known as The Burcey Refining Company. This was in the middle seventies, and the plant is still in operation. It has served a good purpose, and to it was due perhaps more than to anything else the substitution of steam for direct fire distillation.

Before leaving this early history, it should be mentioned that the Turnbull plant, and in fact several succeeding plants, had but four pairs of retorts or 5 cords capacity to the charge; thus by obtaining two charges within 24 hours their total wood consumption was about 10 cords per day. Today there are single plants operating 160 cords daily. Thus we have an illuminating comparison, at least as far as size is concerned, of the development of the industry.

DESIGN OF APPARATUS

Even at the present time, there remain many plants using the old original retort system, with one very slight modification. Those first in service were of cast iron, while the later ones have shells of steel with riveted cast-iron necks and fronts. The purpose of this change was due to the fact that in the early operations, since the wood was then of much less value than later, and high yields were not so important, it was charred at a very high temperature, in order to increase as much as possible the capacity of the plant by shortening the time of firing. As cast iron was much more durable for these high temperatures than steel, the use of cast-iron retorts was universally practiced. When, however, with the coincident rise on the cost of wood, it was found that lower temperatures gave an increase of all products, it was seen that steel could be employed to advantage, for its lower weight permitted the turning of the retort. This turning refers to the saving in apparatus universally practiced and consists merely in the removal of the brick setting when the side in contact with the fire becomes buckled, rolling over the retort and placing the uninjured part next the fire, thus materially increasing the life of the retort. This modern retort is of uniform size and design in all plants which still use this type of apparatus. The shell, as originally, is 42 in. in diameter and 9 ft. long, supported at the ends in a cast-iron cradle and having a cast-iron front, with door and lugs, for pinning the door shut. At the rear is a neck 10 in. in diameter, to which is attached the condenser.

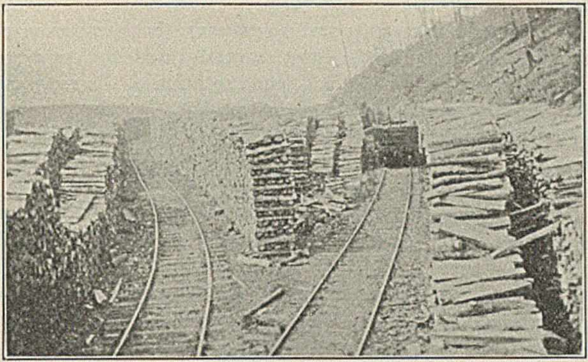
The evolution of the condenser is especially interesting, in view of the fact that when the original condenser was installed each succeeding plant accepted it as being of proper size, and the new installation was made the same size. Then from time to time some one would discover that an addition would yield more product and at once the arbitrary sized unit was changed. Originally the worm condenser was used, but it soon became apparent that the heavy carbon bodies caused clogging, and soon the log condenser was substituted and was used until the introduction of the upright tubular one. These log condensers were made by attaching, by a copper tee, a large-sized copper pipe, called the log, to each of a pair of retorts. Near the ends of this pipe were copper connections, joining the large log to a smaller one, and this in turn was similarly connected with others progressively decreasing in size. The whole log condenser lay in a plane at an angle of 45° and the whole was surrounded by a wooden box with water inlet at bottom and outlet at the top. The joints were simply slip joints and were slipped together and "sweeled;" that is, wrapped with a cloth liberally covered with red lead, which, after becoming dry or "set," offered a suitable and effective joint. At the ends of the logs were removable slip joint caps, for cleaning purposes, so that the cleaning from the heavy tarry and carbonaceous bodies was easily accomplished.



ANCIENT TYPE OF COPPER STILL—IN A NOW DISMANTLED RETORT PLANT. FORMERLY DIRECT FIRED, THEN CONVERTED TO STEAM HEATED

The first really important change in the general style of operation was that of replacing the old retort by the oven, which was done in the middle nineties and is claimed to have been first tried out at Straight Creek, Pa. This change was wholly mechanical, and consisted merely of substituting for the retort a large rectangular oven, equipped with rails on the bottom for the purpose of carrying cars. These cars were loaded with wood and could be quickly pulled in and out mechanically and the charcoal unloaded outside the oven, greatly increasing the economy in this part of the operation, over the slow hand drawing of the charcoal of the retort system.

There appear to be, however, many more advantages in this style of operation than the mechanical advantages which were at first anticipated, as an increased yield of products is obtained, due undoubtedly in part to more advantageous manipulation, but in our opinion also to the different chemical reactions that take place. In the old retort system complete carbonization of the wood took place in about 16 hours, and it required in the oven system 24 hours; yet the temperature of the gases at the neck are higher in the latter, running at a maximum under skilful manipulation to about 330 to 360° C., while in the former case the operation was consummated at not over 290° maximum. This maximum temperature is obtained about midway, or two-thirds, of the run, at which time a very decided exothermic reaction takes place, and care must be exercised that the liquor is not "burned;" *i. e.*, that the temperature is not permitted to rise. If this happens, undue formation of condensation products results, which is immediately indicated by an increased flow of gas and a darkening of the crude liquor. This exothermic reaction, which also takes place in coal distillation, probably accounts for the increase in temperature of the uncondensed gases in the oven system, since no greater proportionate radiation takes place in this system than in that of the retort construction. At this particular stage, on account of the nature of the source of heat (exothermic changes in the wood), a much more uniform temperature throughout the oven is maintained. This gives an excellent illustration of the possibility of considerable alteration, even in the chemistry involved in a process, when we change the mechanical manipulation.



Typical Pennsylvania Wood Yard

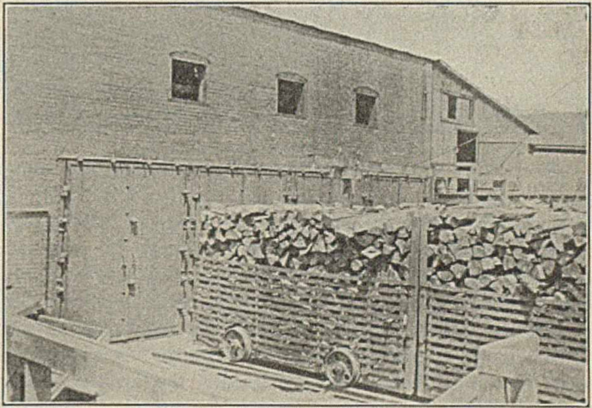
An additional advantage obtained by this oven system is that the charge of residual charcoal may be drawn while the oven is still hot, thus economizing on the fuel necessary for reheating, while a partial cooling is necessary in the hand-drawn retort system. The time lost during this cooling was saved in one design at Dahoga, Pa., where the retort at the conclusion of firing was removed by a crane from its vertical setting and replaced at once by a previously charged retort. It is stated in the meager literature on this industry that "this type is probably most used."[1] This Dahoga installation, though it operated for many years, was the only plant of this type that ever was installed in this country, as far as we are aware, and certainly there is little likelihood of any existing now, for this one was recently converted into an oven plant.

There is still a third system, which should be at least mentioned, namely the kiln system. This was really the second in date of development, but the oven system was so closely allied in design and operation to the original retort system that the two were taken up together. The fact is, we would expect the logical development to have been: charcoal heap—charcoal pit—charcoal kiln—by-product charcoal kiln—retorts—ovens; but this does not appear to have been the case, in this country at least. As in the coke industry, we do not appear to have gone from bee-hive oven to by-product bee-hive oven, directly, but through the by-product oven, an outside and distinct invention. So in this industry, the charcoal kilns were converted into the by-product kiln system only after the development of the retort system.

When charcoal was produced in kilns, from 20 to 86 cords of wood were placed in a kiln constructed of bricks, and wood was used as fuel for carbonizing. The volatile products were lost through the opening provided at the top. With the advent of markets for charcoal and acetate, some charcoal manufacturers placed a pipe connecting this opening with a suction fan and a condenser and thus collected the volatile products. The amount of product thus recovered is but a fraction of that recovered in a retort or oven system. In Pierce's system the flat-topped circular kilns usually hold 50 cords. They are heated by gas burned in a furnace under the kiln. For the sake of brevity, a description of these interesting kiln plants will be omitted since their recovery of by-products is low and they are confined almost exclusively to the blast furnace plants of Michigan, where they are steadily and rapidly being displaced by oven plants.

YIELDS

The low yield from the kiln system, which runs about 100 lbs. acetate of lime and 4 gal. of alcohol per cord, together with the low yields obtained by *rapid or quick* firing, plainly show that there is a mean temperature which gives the maximum yield. Just what the curve of efficiency is, has never been definitely determined in a commercial plant, to our knowledge, though we have given it much experimental attention and others doubtless have worked on it also. In fact, there are so many factors to be considered in a comparison of experimental operations on a commercial scale that while the factors causing increased or lessened results are known, it is difficult to obtain accurate definite knowledge as to just how much each factor contributes to the results. For example, we know that Michigan plants under approximately the same construction and operation obtain less product per cord than those of New York and Pennsylvania, without certain knowledge of the relative influence of the various contributing factors.



Loaded Wood Cars at Ovens

This lack of definite data on a commercial scale, so deplorable in most industries, results from the difficulty of obtaining suc-

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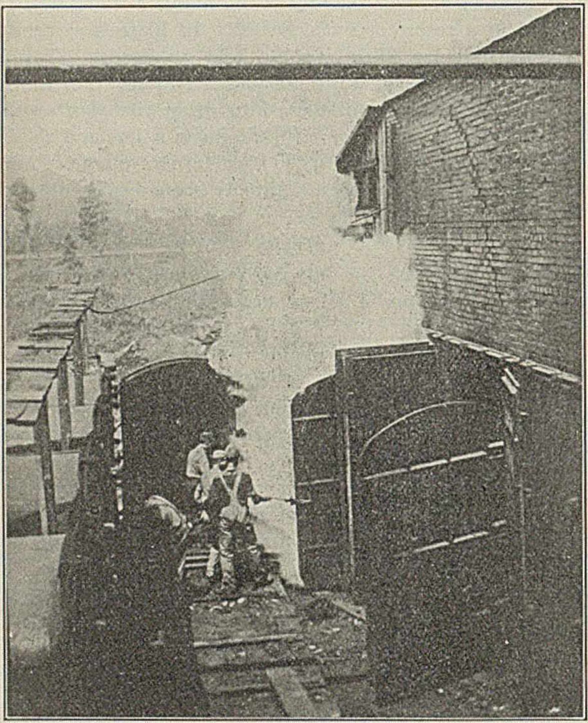
[1] *Met. and Chem. Eng.*, **1910**, p. 155.

cessive tests with all conditions alike, for we well know that any variation, for instance of temperature, has a peculiar relation to the results obtained. In addition, it goes without saying that the variety of species of the wood enters largely into the results obtained, and even the part of the tree used may cause variation. For example, a charge made up wholly of heartwood will give better yields under the same conditions than a charge of slabs, making due allowance for the bark. Again we have found that, weight for weight, cord-wood obtained from the mature or virgin trees will yield higher than the small second growth; also we are convinced of a noticeable difference in results from wood of the same species grown on high and dry places, and that from low or marshy soil, the latter giving a slightly lower yield. Indeed it is interesting to hear the experienced operator maintain that wood cut in the winter months will give better results than that cut while the sap is running. We are, however, unable to verify this expression, and it is possible that some other factor may have been responsible for this often repeated statement. It is also held by many operators that, eliminating the consideration of extra fuel necessary for the charring of green or unseasoned wood, the results are not the same in finished product as from well seasoned wood. We can see from these statements that, with so many factors to be considered, it is extremely difficult to determine which enter most into the discrepancies between the various systems: retort, oven and kiln. However, from the purely practical standpoint we do know that there is a marked difference between yields obtained from the different systems as well as from the two general localities extensively operating.



START OF OVEN PULLING

If we compare the results obtained by the same system operated in the Allegheny Mountains with that of the Lake Superior region, we find that by taking the results on a yearly basis from a well operated plant and calculating the wood on a basis of a cord 8 × 4 by 52 in., there should be obtained conservatively 216 lbs. of 80 per cent acetate of lime, 11.3 gallons of 82 per cent crude wood alcohol, and 52 bushels of charcoal. The yield from the Lake district is slightly under this in alcohol and decidedly so in the acetate yield, which is 175 to 180 lbs. on continued operation. However, here again we have at least two factors and it is difficult to determine their relative influence. First, in the eastern field, beech predominates while in the other hard maple is in larger proportion, and also slab wood is used much more largely. In fact, we have been unable to obtain data from a continued operation in which at least a small proportion of slabs was not used.

CONSTRUCTION

At this point it may be well to take up the question of construction, especially of the most successful and modern system, that of the oven, which is, with the exception of the mechanical manipulation, similar to the retort system.

The ovens are of uniform height and width, in most plants being 6 ft. 3 in. wide and 8 ft. 4 in. high, the length determining the capacity, running from 26 to 54 ft. and holding from five to ten cords. The steel used in the shell is usually $^3/_8$ in. while the bottom and back heads are of $^1/_2$ in. material. Ovens are built either with doors at both ends in order to withdraw the residual charcoal coincidently with refilling the oven with the wood-loaded cars, or in many cases, with a door at one end, the oven being loaded after the charcoal has been run into the coolers. In any event, the door is hung upon a cast-iron frame riveted on the oven. This frame has a groove of about 1 in. for the use of asbestos packing and the cast-iron door is hung to the frame by riveted cast-iron hinges. The oven is stiffened by means of angle irons riveted perpendicularly on the sides, and on one side near the top are riveted 30 in. cast-iron nozzles, usually two in number, to which are attached the condensers.

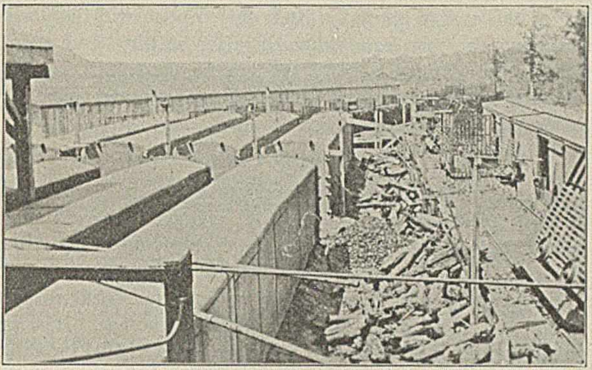
The first ovens installed were placed upon piers in the setting, upon which were iron plates and rollers to accommodate expansion of the oven, but in the later settings the ovens are suspended from Tee rails laid across the brick setting at the top and supporting the oven by means of U bolts riveted thereto. The bottom of the oven is equipped with clips for holding the rails which carry the wood cars. These cars vary but slightly in length in different plants, running from 10 ft. 4 in. to 12 ft. 4 in. inside length and about 78 in. high; thus each car holds from 2 to $2^1/_2$ cords of 52 in. wood. Each has four 18 in. wheels with roller bearings running on $2^7/_{16}$ in. turned steel axles.

Immediately in front of the ovens are two charcoal coolers arranged in series and approximately of the size of the ovens. In the first the hot charcoal is drawn from the retort, where it stands for 24 hours. From this cooler it is drawn into the second one for another 24 hours of additional cooling. These coolers are made of very light iron with cast door frames riveted on each end, and light sheet iron doors. No bottoms are required, as the coolers are simply placed on the ground and banked along the sides and doors with loose dirt.

To the nozzles heretofore mentioned are connected the condensers. These are upright tubular condensers, made with copper hoods having a removable head, and are bolted to gun metal heads which are bored for the copper tubes, usually $1^1/_4$ in. O. D. seamless copper, and expanded into these gun-metal heads, the whole surrounded by a steel water-jacket with water inlet at the bottom and outlet at the top. Connected to a bottom pan bolted on the lower head is a goose-neck trap for trapping off the non-condensable gases, thus separating them from the pyroligneous liquor, which is run into a wooden tank. The gas from the charge is carried into a main gas line which runs to the boilers where the gas is injected under them by a small steam jet. This jet performs the additional and very important function of serving to reduce any back pressure on the ovens, thereby preventing leaks. In order to prevent this suction from becoming too pronounced and drawing over the lighter volatile products through the condenser into the gas line, a butterfly or clapper valve is arranged on the line and regulated by a spring so set that any undue suction opens the valve, thus relieving the line.

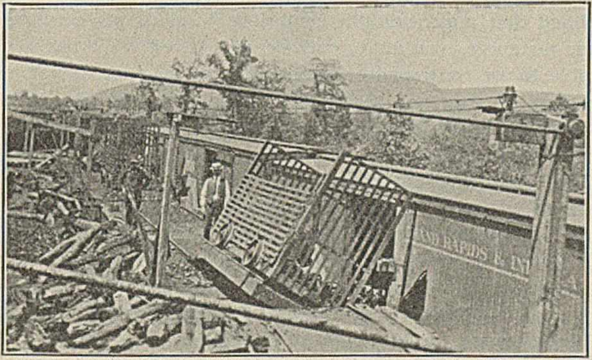
PRIMARY DISTILLATION OPERATION

After this general outline of the first stage of the construction let us follow the operation to this point. After the loaded cars are run into the ovens the doors are pinned shut with taper pins driven into lugs which are parts of the castings of the door frames. The fires are started under the ovens and in about an hour the water distillation and first dissociation begins, the distillate being of a very light yellow color and having a tannin-like odor, and running about 2$^1/_2$ per cent of acid during the first hour when well seasoned wood is used. Gradually this acid content rises until about the fifteenth hour, when the content should be running from 12 to 14 per cent. After a few hours running, a small percentage of light tar begins to appear and steadily increases until at the latter end of the run tar is by far the larger constituent of the distillate. The acid content of the watery constituent gradually diminishes until it is almost negligible.



Charcoal Coolers in a New York Plant

The product obtained under the usual practice, with average wood of at least a year's seasoning, is from 215 to 220 gallons of crude pyroligneous product giving an acid titration of 8 to 8$^1/_2$ per cent and an alcohol content of 4 to 4$^1/_2$ per cent. The tar yield is from 22 to 25 gallons to the cord, with a residual charcoal in the cars of about 52 bushels of 20 lbs. each. With green or unseasoned wood the total distillate is diluted and will run from 275 to 325 gallons of liquid.



Dumping Charcoal

In the early stages of the run the non-condensable gases are largely air and carbon dioxide. Therefore for the first few hours, and even after much of the hydrocarbons and carbon monoxide are accumulating in the gases, they have no fuel value. However, the percentage of carbon dioxide diminishes rapidly, and from the middle to the end of the run the oven gas has an important fuel value. The total amount of gas will run from 11,000 to 12,000 cu. ft. per cord.

As we have already intimated, the influence of the temperature of dissociation is extremely important, and the yields are very dependent upon its regulation, *e. g.*, if, during the height of the run, the temperature at the neck of the oven materially exceeds 750° F. much greater volumes of non-condensable gases are being formed, together with an excessive amount of tar, and it is quite possible to lose from 5 to even 10 per cent of charcoal, together with a serious loss both of alcohol and acid content. Rapid firing, however, without reaching excessive limits, will materially increase the acid content at the expense of the alcohol, while slow even firing, operating the oven at a period in excess of the usual 24 hours, will increase the alcohol production somewhat and lessen that of the acid.

The interesting results obtained from excessive firing arise, as we hope to show later, both from a difference in the chemical dissociation and also from the subsequent formation of condensation products.

In drawing the hot charcoal from the ovens, quantities of combustible gas remaining in the ovens would cause explosion on the opening of the doors. This is obviated by the introduction of live steam into the front of the oven for a short time before the drawing is made.

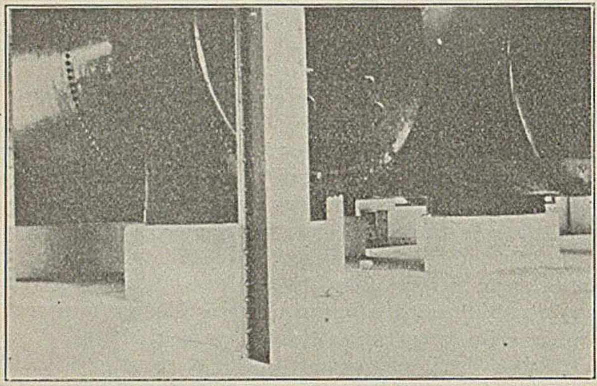
HANDLING THE CRUDE DISTILLATE

The crude distillate or pyroligneous acid, called in the works "raw liquor," is first pumped into a series of wooden settling tubs, connected by brass piping. The first tub, where the greatest amount of tar settles, is connected near its top with an overflow pipe to the second tub. The second tub is connected with the third by a pipe somewhat lower, and this series of drops is continued so that the last tub is drawn from within about 18 in. from the bottom. The raw liquor thus settled free from tar is as a rule continuously run into the copper stills. These copper stills are for the purpose of distilling off the lighter volatile products away from the tars and oils which remained in solution in the settled liquor. They are from 7 to 10 feet in diameter with proportionate height, made of 12 to 14 gauge cold-rolled copper, and equipped with a steam coil, usually of 3 or 4 in. seamless drawn copper tubing starting from about 18 in. from the top and running helically around the walls and on the bottom to midway between the center and periphery. For a 2,000 gallon still, from 300 to 400 sq. ft. of heating surface should be used. In addition each still should be supplied with a live steam jet applied at the bottom and preferably through a copper ring having small steam openings.

After a copper still has run continuously for some time it gradually becomes filled with deposited tar and its flow of distillate diminishes. When this has reached a stage of very slow production, as it does every four days, the feed valve is closed and the live steam jet is opened, distilling the tar with live steam, thus obtaining considerable quantities of acid and light oils. This latter distillate is run into separate tubs, where the light oil on the top is withdrawn before the acid liquor is pumped into the original copper still distillate, which has been run into a wooden "mixing tub." The tar from the settling tubs is usually distilled in a separate tar still, sometimes made of wood, and distilled as has been that just described. This practice is followed as it permits the separation of the oils independently and without allowing them to come in contact with the original distillate, in which a portion would dissolve; thus the bulk of the distillate contains less impurities by this practice.

The mixing tub is usually from 12 to 14 ft. in diameter and 4 ft. high, having a very heavy wooden stirring arm fastened to the end of a heavy shaft, operated by a slow moving gear at the top. Slaked lime is slowly added to the liquor in the tub, which contains its own indicator, the liquid changing at the neutral point to a pronounced wine color. For maximum yields, however, probably owing to the acetic esters present, the addition of lime should be continued until this color has been followed by a yellowish one and until a bead appears or bubbles form on the surface and disappear slowly. A very small further addition of lime at this point causes the acetate to stick to the pans when evaporated and prevents satisfactory crystallization. Under-neutralization also causes inferior quality in crystallization, and before final drying the acetate has a decided black color instead of a rich yellow-brown; also there is an accompanying loss in product owing to the esters lost.

From the mixing tub the neutralized liquor is jetted or run into an iron still known in practice as the "lime lee" still. In a few plants this is equipped with either Burcey pans, or in some more modern works with a fractionating column, although most plants do not fractionate at this point. The customary practice is simply ordinary distillation. The crude alcohol starts over at about 20 per cent on a Tralle scale but quickly rises to 35 and at times 40 per cent, gradually dropping in percentage to from 15 to 20, at which strength it continues for some time and then drops rapidly to 5 or 6 per cent, at which point it seems to hold stationary again for a long period. After all of the alcohol has been distilled over, a valve in the vapor neck is closed and the residual acetate solution is blown, by means of live steam pressure applied in the still, to an iron settling pan above the top of the ovens, where the excess lime and insoluble impurities settle out in a few hours. The acetate liquor is then drawn into flat steam pans having a jacketed bottom for steam supply, the pans usually being about 16 ft. long by 8 ft. wide and 18 in. deep. Here the acetate liquor is boiled rapidly until crystals appear on the surface near the edges, when the steam is reduced so that the crystalline film which forms at once on the top does not break, which would cause it to fall to the bottom and form a hard crust. Care must be exercised in this "seeding" process as it is called, or a great quantity of this exceedingly hard crust or scale will be produced, which is unfit for the market. After this "seeding down" has continued until the whole mass in the pan has reached a very thick mushy consistency, it is shoveled out on the acetate or "kiln floor," which is a smooth brick or tile covered floor over the top of the ovens. Here the acetate is continually turned until dried and ready for sacking and shipment.



Soda Stills—Wood Alcohol Refinery

The "weak alcohol" from the "lime lee" still, containing from 9 to 12 per cent of acetone and alcohol, is accumulated and distilled in an iron still having either 5 or 6 Burcey pans or a column. This distillate is the final crude product produced by the works, and is usually shipped to a central refinery, although a few plants refine their own product. In this distillation all the product coming over above 60 per cent is run into the storage tank, and the lower fraction is put back with the lime lee distillate for further distillation. The finished crude is sold on a basis of 82 per cent and contains about 16 per cent acetone.

Returning to the copper still residue, the tar from these stills, as well as that from the tar still, is run into a sump and from there jetted under the boilers for fuel. The two fuel products, gas and tar, furnish approximately 35 or 40 per cent of the necessary fuel for all operations.

Before leaving this subject of operation it might be said that many of the earlier plants omitted this copper still distillation, neutralizing the raw liquor directly after settling and thereby obtaining the "brown acetate" of commerce, which is today practically without market. This brown acetate runs from 60 to 65 per cent acetate.

PRODUCTION COSTS

The costs of producing the products above mentioned have been on a constantly increasing scale, owing in a large measure to the increasing cost of cord-wood and stumpage. During the past fifteen years, in the eastern district, stumpage in suitable location has been sold for as low as 15 cents per cord, while today 75 cents to $1.00 is the approximate average. The cost of cutting varies from $1.15 to $1.35 per cord in fair timber and in scattered timber $1.50 is sometimes paid. Today, including transportation, piling, etc., this will make the cost on board oven cars $4.00 to $5.00 per cord, though wood is being put in for as low as $3.50 by users of mill-waste or by those having long standing holdings.

This gradual rise in the cost of wood is due to natural causes, among which are the increase in stumpage cost due to the ever-decreasing supply, and the natural rise in labor, together with increased length and cost of transportation. With the exception of one possibility, there appears to be no hope of any future lowering of costs. This one exception, a new cord-wood splitting machine, appears from our examination to have merit, and presents an entirely new system of cord-wood production. It is generally conceded that cutting and hauling the large log is less expensive than cutting and handling the cord-wood at the stump. The tree is therefore cut in logs and large limbs and transported to the machine, where a slide carries it first to a cross-cut saw, which cuts it into the proper lengths. The sawed pieces continue to a platform where they are either split in halves or quartered by one blow. The split wood automatically moves by a slide to the railroad car or wagon. It is claimed that under suitable conditions 50 cents per cord, or in some instances even more, may be thus saved. We have been unable to see continued operations of this machine as yet, and consequently can not verify this saving cost, but are inclined to believe that at least some reduction in wood cost is possible by this means.

The cost of fuel for a crude works, in addition to the tar and gas used, of course varies with the available supply. In the New York and Pennsylvania districts, when coal is used, this cost will amount on an average to $1.15 per cord, and when natural gas at 15 cents per 1000 cu. ft. is used the cost is but slightly more. The labor at the plant is usually counted at $1.25 per cord.

The following summation of production costs will be generally accepted as a fair basis in considering investment in new installations.

Production Costs per Cord of Wood

Wood (maximum) per cord	$5.00
Fuel	1.15
Labor	1.25
Lime, 0.96 bu. at 19 cents	0.18
Bags (acetate)	0.14
Freight (acetate) 16 cents per 100	0.35
Freight (alcohol)	0.10
Selling commission acetate	0.11
Insurance 0.068 per cord Taxes 0.112 per cord General expense	0.57
Total	$8.85

PRODUCTION VALUES

With the present slump in markets the values herein set down are low, especially that for acetate of lime. The past 10-year average would be about \$2.00 per hundred, while at present the market is slow at \$1.75 per hundred.

Alcohol (82%), 11 gal. at 25 cents	\$2.75
Acetate of lime, 216 lbs. at 1.75	3.78
Charcoal, 52 bu. net at $6^{1}/_{4}$ cents	3.38
Total crude value	\$9.91

This gives a production cost of \$8.85 and a sales value of \$9.91 per cord. It will be noted that no selling costs except in the case of acetate of lime have been included, because, in the works not refining or making the finished products, which are in number far in excess of those who do refine, the alcohol is sold under contract to the refiner, and the charcoal is either, as in the case of those plants in the Lake district, consumed at iron furnaces in connection with the plants, or as in the eastern field handled by a general sales agency controlled by the manufacturers, proportionately to their daily production capacity, yielding to the producer about the above-mentioned figure at present.

These production costs are based on the yields in the eastern field, which as pointed out were higher than those of the Lake region. This discrepancy is compensated, however, by the fuel and wood costs being lower in the Lake region, owing to the fact that in most instances mill-waste is used. The general relation between the two fields of operation, in this production cost and product value, is therefore approximately the same. It is undoubtedly true that many manufacturers can show much greater net profit than the above figures indicate, because of cheaper wood and fuel and in some instances because of plant design.

COSTS OF INSTALLATION

Eliminating the cost of wood supply, \$2000 per cord per day production is counted as a reasonable installation cost for a plant as described, for producing crude products. For instance, the cost of boilers, ovens, cars, coolers, pumps, etc., is substantially \$650. Copper work, including stills, condensers, piping, etc., approximates \$450. Brickwork for ovens and boiler settings, etc., will come to about \$190. These three general items are more or less about a fixed estimate, varying of course somewhat upon the price of materials at the time. The location, buildings and general costs vary with the design and the desire of the builder. However, the above stated general figure of \$2000 is a fairly accurate estimate, unless elaborate construction is undertaken.

LARGE SCALE EXPERIMENTATION

Realizing the possibilities and necessity of counterbalancing the increasing cost of production, several large operators have made extensive large scale experiments with a view to increasing yields and lowering production costs. Unfortunately the results obtained thus far have not justified the expenditures made, in spite of many optimistic claims,[1] owing in a measure to the many unlooked-for complications which arise between the laboratory and the works scale. Of the great amount of work which has been done along this line with which we happen to be familiar, space permits the citation of but a few illustrative instances.

In the fall of 1908 certain men largely interested in the business went to Germany to investigate developments there and returned with a process for eliminating the copper stills and making gray acetate of lime directly from raw liquor, a proposal which had already been made and studied in this country. This process had been reputed to be in successful operation in Germany. It was in fact merely the application of the cup column to the neck of the ovens. The cups and openings were of course of larger size than in the customary column, but in effect this really was all that could be claimed for the new appliance. It was held that the pyroligneous vapors, passing through the condensed tarry liquor, were freed from their impurities by this means and that gray acetate could be produced from the resulting raw liquor by direct neutralization. Educated or impressed by the then incomplete American investigations mentioned, these men permitted themselves to be carried away by the assurances of the German engineers and, as has happened several times in our industrial chemical development in more or less identical circumstances, without any experimental investigation they equipped a large plant with this apparatus at an enormous expense, the copper work for which alone exceeded \$80,000. The plant did not prove satisfactory.

It will be at once seen from foregoing statements in this article, that there were two fundamental reasons which explain, in our opinion, the failure to obtain the desired results. *First,* as pointed out, mechanical clogging of the apparatus would occur, as was the case in the original worm condenser; and *second,* as we believe, the valuable products readily form condensation products with the unsaturated hydrocarbons and aldehydes present in the distillate. Certainly the passing of these vapors through the hot tarry liquid would tend to increase this chemical reaction. Moreover, the apparatus caused back pressure on the ovens and required a suction to overcome this objection. This increase of suction would tend to bring the vapors through the cups and the condensers at a more rapid rate, which of course would lessen their efficiency.

Later another process, also brought from Germany, was tried, which was in effect the same as the one above described, except that the vapors were forced through a body of hot tar for the purpose of washing them, but this also was not successful. In our opinion this failure was for the same fundamental chemical reason as mentioned above.

A process for accomplishing this result, but not as yet entirely developed, from which some very satisfactory results have been obtained, is based upon a totally different theory from those mentioned. This method places a fractional condenser on the neck of the oven, which is maintained at a temperature sufficient to liquefy the high boiling tars and oils. These, however, are largely mechanically carried along by the uncondensed and non-condensable gases, while a part of the tar is run off through a gooseneck on the bottom of the fractional condenser; the uncondensed vapors and the non-condensable gases with their suspended tar and oil liquids are carried into the bottom of a centrifugal basket or drum, installed in a copper container and having small perforations inside of the drum, which is supplied with wings to give a rapid motion to the gases. This centrifugal action throws the liquid particles or mist against the side of the container, on which are deflectors set at an angle opposite to the direction of the moving drum. Thus the condensed bodies are forced to the bottom of the container and out of the zone of circulation, through a gooseneck into the tar receiver, while the vapors continue to a second condenser where they are condensed, the wood gas being trapped off in the usual manner.

This process has given uniformly increased yields of product but exact data as to saving, yields and cost of operation have not been determined as yet. A little over 1 H. P. is necessary for the operation of a 7-cord machine until speed is attained; then $^{3}/_{4}$ H. P. is necessary.

The increase in product yield with this method is probably due to the fact that the vapor contact with the condensed and unsaturated bodies present is reduced to a minimum.

Another attempt at fuel conservation, which it seems should be possible of accomplishment, relates to the evaporation of the acetate liquor. As has been seen, much heat is necessary for this evaporation, and this method attempts to utilize the high

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[1] *Met. and Chem. Eng.*, **1910**, p. 434.

temperatures of the gases at the oven's neck before they enter the condensers. We are not aware of any installation of this nature although patents have been issued for accomplishing this end. Nevertheless, as it involves what appears to be a wholly mechanical manipulation there should be no great difficulty in saving at least a portion of this waste heat. Here again it can be seen that experimentation to accomplish this end is costly, since all experimental changes necessitate considerable financial outlay if tried on a large oven, and also involve interruption of regular operation which must from time to time inevitably occur.

Under this head of experimentation may properly come an elaborate attempt to utilize hardwood sawdust for alcohol manufacture. This was undertaken in 1903 by a well known lumber company in Cincinnati, who endeavored to destructively distil sawdust continuously by means of an endless belt which carried the sawdust through an oven for the purpose of carbonizing, tapping off the pyroligneous vapors and obtaining an uninterrupted production of charcoal, which was briquetted. The distillate was handled in the usual manner.

It can be readily seen that sawdust can not be destructively distilled in bulk, as is cordwood, for the insulating space between the particles prevents the heat from going through the mass. This explains the reason for the endless belt.

No expense was spared either in buildings or equipment, the buildings being of stone and the equipment of the best, the whole costing probably $200,000. Notwithstanding this outlay, the operation was a complete failure, the plant being dismantled within a year and the buildings used for other manufacture. The high fuel cost in attempting to overcome the resistance to radiation in such a mass was an important item in the high production cost which resulted in the failure. In addition, sawdust charcoal is a more dangerous fire-risk than common charcoal, in the handling of which in the ordinary plant, special arrangements are necessary.

Within the past five years some plants have installed double and triple effect evaporators with a view to fuel economy, and reports as to the results are very contradictory, but the continued use indicates at least partial success. One Michigan plant is successfully drying its acetate with a drum and belt drier. Vacuum drying for acetate has been tried, but we are unaware of any success as the resultant product is a powder, while the market demands the crystal.

REFINING

From the time of the formation of the already mentioned Burcey Refining Company, the usual plan of manufacture contemplated only the production of the crude product as described, selling the products, those of the Eastern field, largely to a Buffalo refinery and the Michigan manufacturers to Detroit. Up until the passage of the Denatured Alcohol Bill by Congress they received a price usually ranging from 40 to 75 cents a gallon for the crude alcohol. After the passage of this act, and with the purchase of the Detroit plant by the one at Buffalo, the price of crude was at times as low as 15 cents per gallon, and during this period of adjustment intense depression prevailed among the crude producers, as it was feared that ethyl alcohol would largely supplant methyl. It was found, however, that the trade, particularly the paint trade, preferred wood alcohol even at a slightly higher price, and this fact virtually saved the industry. With the formation of a refining company among eastern crude operators representing somewhat over 1,000 cords daily production, and the erection of a refinery at Olean, N. Y., the monopolistic control of refining was immediately reduced. A very acceptable dead rental was paid to the crude producers for their uncompleted refinery, as well as a substantial increase for their crude product, which eventually reached and is maintained at about 25 cents per gallon of 82 per cent product.

The method first employed by refiners was merely that of fractional distillation, and we all perhaps remember the yellow, ill-smelling wood alcohol of commerce. Later, and for a long time, bleaching powder and sulfuric acid were used before the final distillation. This materially improved the product, but with the improvement of the columns used, treatment with sodium hydroxide and distillation is all that is necessary. The NaOH serves the purpose of polymerizing the aldehyde impurities and saponifying the tarry matter. The esters present are also affected. The formerly objectionable acetone present, which distilled with the heads, now has its own market value under the name of acetone-alcohol and is used in varnish removers, as a solvent in the rubber and other industries and also as a carrier for acetylene gas in lighting systems. Thus this 16 to 18 per cent of impurity is now in fact an added value to the refiner.

MARKETS

Prior to the present unfortunate European situation, the average production of acetate of lime from the manufacturers in this country amounted to approximately 7,000 tons monthly, and we are informed that the total European and Canadian production is almost equal to this, of which tonnage Austria-Hungary furnished about two-thirds. The plants in Europe, however, are usually on a very small scale in comparison with those in this country. Sweden alone has plants of a size in any way comparable with the larger ones here. Of the production of acetate in this country, from 50 to 60 per cent is exported, a considerable percentage to or through Belgium. Of course, it will be understood that these statements refer to the market situation before it became demoralized by the European war, although for a year prior to the declaration of war there had been a pronounced stagnation of the markets both at home and abroad.

Of the acetate of lime consumed in this country, by far the largest percentage goes into acetic acid production. The hardwood industry is therefore vitally connected with this acetic acid industry, and one of the most important developments in the last decade is the successful beginning made in combining the crude manufacture and this refined product manufacture in the same plant. Such combination plants have shown crude acetic acid yields in continuous operations running 92 to 96 per cent of theory using 5 per cent sulfuric acid in excess of that theoretically required, and giving on a continued daily production of 4,000 lbs., with a yield of 91 per cent of the possible theoretical yield, refined acetic acid of the finest double distilled quality.

The chief individual acetic acid market demands in this country are from the manufacture of white lead, paint colors, and the textile and leather industries, although in the aggregate the small consumers, such as the laundries, ink and drug trades, use great quantities. This country prohibits the manufacture of acetic acid vinegar but its production is permitted abroad.

The consumption of export acetone produced in this country is chiefly by England, and Italy is just now a large consumer. The industry is in a particularly thriving condition at the present time, owing to the use of acetone in production of explosives for the European war. There should be obtained 20 to 22 lbs. of acetone per 100 lbs. of acetate used, and in connection with the crude works acetone production is very profitable, as the general operating expenses are low. Of course its use in this country was very large for explosive manufacture and for the production of chloroform under the well-known Rump patents, regarding which there was so much patent litigation some years ago and which as you know were upheld. In comparatively late years, however, a large Michigan concern has produced chloroform commercially from carbon tetrachloride, which has probably influenced somewhat the acetate consumption for this manufacture. There are 4 plants in the United States producing acetone for the market and within the past week ground has been broken in Pennsylvania for a 5th plant. There is but one plant operating in Canada to our knowledge.

Ten years ago the steel industry consumed by far the major percentage of charcoal produced. This percentage, however, has decreased considerably, owing to the improved methods for steel production. Many industries such as cutlery and car wheel manufacture demanded charcoal iron, but in these and many other instances coke iron has been substituted. This falling off in the proportionate use of charcoal in iron production has been made up in an increased domestic demand. Charcoal is now sold in small paper sacks in many cities for use both in hotels and private families.

The production of crude wood alcohol amounts to between 10,000,000 and 11,000,000 gallons per year, and of course it has innumerable uses, including those of the paint industry which is the largest single user.

Space will not permit, in a general article such as this, of going into details regarding production and markets of the other products such as formaldehyde, creosote, etc., which are directly or indirectly derived from hardwood distillation.

DISTRIBUTION OF PLANTS

Although not in agreement with any published figures, we place the distribution of distillation plants as follows:

	No. of Plants			Cords Daily			Total No.	Cords
Location	Oven	Kiln	Retort	Oven	Kiln	Retort	Plants	Daily
Michigan	8	..	..	1032	..	...	..	..
	..	5	..	..	1050	...	13	2082
Pennsylvania	33	..	..	1424	..	...	...	..
	..	..	13	..	..	215	46	1639
New York	7	..	..	256	..	...	...	..
	..	..	17	..	..	362	24	618
Wisconsin	2	..	..	96	..	...	...	..
	..	1 (oven-kiln)			250	...	3	346
Kentucky	1	..	..	20	..	...	1	20
West Virginia	1	..	..	49	..	...	1	49
Tennessee	1(a)	..	..	32	..	...	1	32
Vermont	..	..	1	..	..	16	1	16
TOTAL IN U. S.	53	6	31	2909	1300	593	90	4802
Canada	9	..	..	424	..	...	...	..
	..	..	1	..	..	48	10	472
TOTAL IN AMERICA	62	6	32	3333	1300	641	100	5274

(a) A recently constructed 16-cord retort plant now being converted into an oven plant.

These figures will mean more if we remember that 5,000 cords of wood represent a pile 4 ft. high 52 in. wide and 7.5 miles long weighing when seasoned approximately 10,000 tons, thus showing the importance and size of the industry in this country.

CONCLUSION

It will be evident that the chief economic drawback in the present manufacture is the fact that most of the plants do not manufacture the finished products; thus in general it may be inferred that two sets of freight charges, commissions and handling expenses are required before the products reach the consumer. For instance, with acetate of lime at $2.00 the net return to the producer is about $1.75 per hundred. A large part of this difference could easily be saved by manufacturing the finished product at the crude plants.

Hitherto such combinations of crude and finished product manufacture have been thwarted in the majority of cases by an almost complete monopoly of the finished products by certain groups of chemical manufacturers, who by various manipulations maintained control of markets, or who were able to dominate the situation, as in the case of acetic acid, by their regional control of sulfuric acid manufacture, or even attempted control of pyrites importation. The violent market fights which have developed because of these facts have been carried through successfully in more than one instance by the crude manufacturer, because of his advantageous situation and it is certain that these attempts, therefore, to thwart the natural economic development of this industry will sooner or later collapse to a great extent, or the refiner will be compelled to either go into the crude business himself or combine with the crude manufacturer.

We have attempted to show the difficulties met and the expensive experimentation that has been undertaken in the past for the improvement of this industry, and have pointed out some of the results thus obtained. When it is remembered that German statistics claim that but one of 15 serious trials of new chemical processes are successful and that this percentage amply pays for the losses entailed in the 14 unsuccessful ones, it can be seen that while these expenditures are individually unfortunate, in the aggregate this law of averages will probably hold good in the development of this industry, for its economic position demands the solution of the problems indicated.

COLUMBUS, OHIO

DISCUSSION

By H. O. Chute

I am sure the thanks of the Institute are due Messrs. French and Withrow for this contribution to the history and present status in the U. S. of wood distillation and the presentation of the large number of illustrations showing actual present working plants.

While much has been previously published on this subject it has in most cases been by those familiar only with the European situation or who had been consulting European works of the subject.

It is a singular fact that most of the places named as sites of the first works still have working plants and the people and firms then engaged are still in the business. This indicates that the location of a wood distillating plant is not a temporary affair but that the wood supply usually lasts for a generation.

While the statement is true that the carbonization is an exothermic reaction yet the phenomenon is not observed unless the wood is fairly dry, *i. e.*, with from 15 to 20 per cent water. With excess of water the heat disengaged is not sufficient to evaporate the water so there is no progressive action toward the center of the retort except as produced by the fire, and the transmission of heat to the center of the retort from the walls is difficult. This shows the necessity of having dry wood for successful work. Owing to this exothermic reaction the control of the temperature inside the retort by any method of heat insulation or surrounding thermal baths is foredoomed to failure.

While the first operators brought over the Scotch methods yet later arrivals including Burcey, brought over the French methods as then and now practiced. The Burcey pans are merely the French Pistorius pans used in the rectification of grain alcohol and the Otto plant of vertical retorts located at Sargeant near Dahoga, Pa., which has been described, was built by Burcey on the French system. These worked successfully for many years though they were never duplicated in this country.

It must be remembered that wood distillation in the U. S. has developed along two different lines. The charcoal iron industry was introduced at a very early period, in fact shortly after the settlement of the first colonists and this necessitated a supply of charcoal. No attempts to save any of the by-products were tried or accomplished till Dr. Pierce introduced his system of sucking off the smoke or vapors from the kilns with a fan and recovering the alcohol and acetate from them by condensation. With the large amount of charcoal necessary to supply the furnaces and with wood plentiful and labor scarce it became advisable to use kilns; these can use green wood and wood in the form of logs and quite rough, while the retorts required the wood to be carefully cut and split to a six-inch face and dried for about a year.

It is erroneous to state that a portion of the wood is burned in the kilns to support combustion as it is the gas which is evolved that is burned. This may be observed in an ordinary grate fire as the flame comes from the gas while the wood is not consumed till charcoal is formed which gives a flameless combustion. The Pierce system originally contemplated the forcing of the gas back into the kilns after condensation but it was soon found that the gas could not be circulated indefinitely, so that now the kiln is heated entirely by starting a fire inside it and admitting a regulated amount of air to burn a part of the evolved gases so as to generate the balance. For this reason the by-products are partially burned.

It may be said for the kiln process that while it produces only about one-half the amount of by-products it produces an equal quantity of charcoal and it produces more dollars in profits per dollar of investment than the retort process. It has been said that the western works do not produce a corresponding amount of acetate compared with the alcohol, but they do not distil the tar nor the acid as thoroughly as do the eastern works.

The original installation for sawdust carbonization at Cincinnati consisted of tall vertical narrow retorts much like those used for bone char work and with revolving cones inside attached to a central pipe perforated to allow the escape of the gases evolved. These were led out at the bottom but the outlet was soon closed with tar and charcoal dust. The idea of taking the gases out at the top never seemed to occur to the operators.

If any system of conveyors for carbonizing the sawdust was used it must have been well toward the end of the work. This installation was made at a cost of about $125,000 by one who had worked on the problem in Canada for a number of years and spent much money there. Every condition was favorable as the sawdust was from kiln-dried lumber, but the project was an absolute failure and should serve as a warning.

Shortly after 1900 the retort process was established in the west in connection with the sawmills. These sawmills working on hardwood will furnish about a cord of wood from the slabs and rough logs for every 1000 ft. of lumber sawed and the sawdust and offal will furnish enough fuel for the retorts and chemical works. When wood distillation is thus carried on as a by-product of lumbering operations it is evident that the cord wood will not cost $5.00 per cord nor the fuel $1.15 per cord, and these combination plants will therefore probably survive in the struggle for existence. The extreme conservatism of those connected with this industry is shown by the fact that nearly all the plants now use practically the same apparatus and methods that were introduced by the foreigners who first came over. The small round retort has, however, been superseded by the oven, those holding about ten cords each being most popular at present. These ovens are so built that the wood is handled in two-cord cars and the cars are usually handled by a locomotive in large works. The charcoal is also handled and cooled on the same cars and there is little breakage. Some improvement has been made in the west in the method of treating the liquors for alcohol and acetate. In 1905 a process was introduced for making alcohol by distilling the crude liquor in a continuous column still producing alcohol of 25 per cent strength from acid containing 2 per cent. On standing, the oils separated from this weak alcohol and an excess of alkali was then added which polymerized aldehydes and ketones. With another distillation through a similar continuous still it was possible to produce 85 per cent alcohol perfectly miscible with water. In 1906 a multiple effect evaporator was installed which was operated with exhaust steam from the blowing engine of the blast furnace and the acid was distilled in one vessel to purify it, then neutralized and run into the other for concentration; the heat of the condensing acid vapors furnished heat to evaporate the acetate solution.

These installations were made at Ashland, Wis., and the processes were covered by patents Nos. 824,906 and 835,501; shortly thereafter nearly all the kiln plants adopted the above method for producing alcohol and a number of them have also adopted the multiple effect process for handling the acetate. Of late years several modifications of these processes have been introduced but they have not yet operated a sufficient length of time to prove their worth.

It is a singular fact that although wood alcohol is always distilled over alkali, yet the ethyl acetate is only slightly decomposed as the so-called "acetone alcohol" or "methyl acetone" from the heads of the runnings will contain about 40 per cent acetone, 40 per cent methyl acetate and 20 per cent alcohol with specific gravity corresponding to 82 per cent alcohol and a boiling point of 55.5° C. The presence of alcohol acts as a protective solvent.

In conclusion, it may be remarked that the American industry has reached a high state of perfection in the mechanical handling of materials and economical machinery. The production of wood alcohol and acetate has reached a state where more cannot be economically produced from a cord of wood. The quality of refined alcohol on the market is satisfactory and the highly refined grades are nearly C.P. The manufacture of such secondary products as acetone, formaldehyde and acetic acid is carried on successfully at some wood distillation plants.

The manufacture of formaldehyde has proved successful at some places. The manufacture of acetone should logically be at the works, thus saving freight as 5 lbs. of acetate are required for making a pound of acetone. Chemical engineering sometimes consists largely in the study of freight rates. The manufacture of acetic acid has been attempted at a number of works and abandoned though at least one plant still makes large quantities.

Acetate of lime is perhaps the most convenient method of shipping acetic acid and the manufacture nearer the market seems more logical.

The only product which is wasted is the tar. About 30,000,000 gallons of wood tar are burned under boilers every year to get rid of it. Its utilization holds out as much promise as the utilization of coal tar, but with the exception of some light oils which are used in dissolving nitrocellulose there are no valuable products made. Yet we import nearly two-thirds of the creosoting oils we use for timber preservation and as it is probable that the wood creosotes are as valuable as the coal tar creosotes for this purpose, we may hope that this industry will soon develop.

197 Pearl Street, New York City

INDUSTRIAL USES OF HYDROFLUORIC ACID[1]

By K. F. Stahl

The larger works on Chemical Technology[2] give the following uses for hydrofluoric acid:[3]

1—Liquid or gaseous hydrogen fluoride is used for etching glass. The liquid acid leaves a smooth transparent surface, while the gas leaves a rough opaque surface.

2—Hydrofluoric acid in connection with fluorides of the alkalies and some other additions, such as acetic acid or sulfuric acid and others, are used for frosting glass. For this purpose there is in general use a solution of acid ammonium fluoride in hydrofluoric acid. This has the trade name of "White Acid" and contains about 32 per cent NH_4FHF and 20 per cent HF. It works very quickly, *e. g.*, the frosting of electric bulbs requires only about a minute.

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[1] Presented before the Pittsburgh Section of the American Chemical Society, October 15, 1914.

[2] Dammer, Molinari, Ed. Thorpe and Henri Moissan.

[3] It is generally known that hydrofluoric acid produces very painful inflammation if allowed to come in contact with the skin. The remedy usually recommended is washing with water and then with dilute ammonia water. This is effective only with weak acids; with stronger acids, particularly the 60 per cent, washing alone, even if done immediately, does not prevent inflammation, but if the washing is continued for about half an hour by holding the affected part under flowing water the bad effects will be prevented or at least materially reduced. Washing must, of course, begin at once after the acid has come in contact with the skin. Very dilute acid, *i. e.*, up to 5 per cent, produces no ill effect by temporary contact with the skin.

3—In the manufacture of spirits from cereals to retard the development of certain bacteria. The yeast is gradually rendered immune to the effects of the acid or its salts, so that the yeast itself is not harmed, but the bacteria which cause the formation of lactic or butyric acid are killed; thus a purer product and a larger yield are obtained. Very small amounts of hydrogen fluoride are sufficient. Effront, who worked out this process, recommends from 5 to 10 g. hydrogen fluoride per 100 liters of mash. It is not used in the manufacture of whisky, as it is feared that it may have an influence on the flavor. This seems to be well founded, as the flavor of whisky is at least partly due to ethers of the fatty acids.

Ammonium fluoride is, however, used in the fermentation industry to sterilize vessels and rubber hose. But these are always carefully washed with water before they are used again.

4—For the preparation of hydrofluosilicic acid and its salts. (Moissan.)

5—To remove alkalies from the juice of sugar beets. (Thorpe.) This is probably only a proposal and it is not likely that it has ever been carried out on a large scale.

6—To remove silica and silicates from ground anthracite to be used for the manufacture of artificial coal for electrical purposes. This process was carried out for some time on a large scale by F. v. Hardtmuth,[1] but was finally abandoned again as too expensive.

7—To purify crude graphite.

8—For treating earthenware vessels to render them more porous.

The last two uses are mentioned by Prof. Prior[2] in 1903, but I could not find any details in the literature.

9—In dyeing, the antimony acid fluoride[3] is used as a substitute for tartar emetic.

10—To remove substances which have been added to silk to make it appear heavier. (Dammer.)

This process is probably used only in the laboratory in the examination of silk fabrics.

11—In the laboratory, to dissolve and to remove either free or combined silicic acid.

12—To clean sand from cast iron and to remove obstructions from natural gas or oil wells.

I have not learned how much the last named use of hydrofluoric acid is practiced.

These last two uses are apparently not practiced in Europe. They are mentioned in some of the works on chemical technology, but these all refer to an article published by myself[4] in 1896.

To those uses which have been made known through different publications, the following four, which as far as I know have not been published but are in use in the United States, can be added:

I—CLEANING CASTINGS AND STEEL PIPES

Besides for cleaning cast iron, the acid is also used in large quantities either alone or mixed with sulfuric acid to clean steel pipes to be used to enclose electrical conduit wires. It is also very useful for cleaning brass and similar castings.

The particular advantage over other methods for the same purpose are: 1—This acid dissolves the sand direct, while other acids only loosen it and cause it to drop off by dissolving the metal underneath. Hydrofluoric acid also dissolves the magnetic iron oxide (Fe_3O_4) more readily than sulfuric acid or hydrochloric acid. 2—Hydrofluoric acid leaves a cleaner surface and does not penetrate into the castings as other acids seem to do. If castings which have been cleaned with sulfuric or muriatic acid are well washed and dried and afterwards covered with metal or lacquer, it happens quite often that the latter are injured by excrescences starting from the metal.

In cleaning pipes for electrical conduits only the inner side is of importance; it must be perfectly smooth, so as not to injure the covered wires when they are pulled through. On the inside of metal pipes there are patches of melted slag. These can be removed with sulfuric or muriatic acid only by losing considerable metal. This slag, being a silicate, and the magnetic iron oxide, are dissolved directly by the hydrofluoric acid. Frequently a mixture of sulfuric and hydrofluoric acids is used for cleaning such pipe.

Cast steel can rarely be cleaned to advantage with hydrofluoric acid, because the loom used for moulds is baked very hard and dissolves very slowly in hydrofluoric acid.

Castings and pipe are cleaned in the following manner: The acid is used in varying strengths, according to the condition of the material to be cleaned and the available time. One part 30 per cent hydrofluoric acid is mixed with 4 to 40 parts of water, which gives a solution containing 6.0 to 0.7 per cent hydrofluoric acid. The weaker acid is preferable if enough vessels are on hand to leave the castings in the acid pickle sufficiently long. It requires about 12 hrs. to clean castings with 1 per cent acid. Comparatively more acid is required if stronger acid is used, but the time of cleaning is reduced.

Round or square wooden tanks without any protective covering are generally used. For economy in handling small castings they should be placed in a second wooden vessel perforated on the sides and slightly smaller than the first one. This has the advantage that the sand which falls off remains on the floor of the inner vessel, is lifted out with it and is thus removed from further action of the acid. The inner vessel together with the castings can be dipped directly in the wash water.

Heating accelerates the action of the acid bath, which can be used repeatedly if for every fresh batch of castings about $^1/_3$ of the amount of acid originally used is added.

If the castings are to remain bright they should be washed with hot water as soon as they come out of the acid pickle, so that they dry off quickly; otherwise they can be washed with cold water. To the last wash water some milk of lime is usually added to prevent rusting.

II—POLISHING CUT GLASS

Under the published uses of hydrofluoric acid, the one for etching glass was mentioned first; but it is very strange indeed that the use of strong hydrofluoric acid for *polishing cut glass*, which has been in practice here for a number of years, is nowhere mentioned. It started about 18 years ago and is at present probably in use in all of the cut glass factories in this country of which there are quite a number and some of them rather extensive. At first some manufacturers claimed that glass treated by the old process had a better polish. They were soon convinced, however, that cut glass polished with acid had a finer luster and sharper edges.

The last operation in manufacturing cut glass is the polishing of the surfaces which have previously been cut into the glass. This was formerly done with oxide of iron or oxide of tin. As every plane had to be polished separately by skilled labor it was slow and expensive work.

A finer polish is now obtained in the following manner: For vases and similar shapes, where the polish is required only on the outside, a wooden stopper is cemented in water-tight with paraffin or wax. Other surfaces which are not to be touched by the acid are also covered with asphaltum, wax or some similar substance. It is essential that all surfaces to be polished must be absolutely clean, and especially free of every trace of grease. To accomplish this, they are brushed with soda solution by girls who wear rubber gloves, then they are washed in clean water and after most of the water has dripped off they are dipped in the acid bath.

Generally a mixture of one part by weight of sulfuric acid, 66° Bé., with three parts 60 per cent hydrofluoric acid is employed. This mixture is in a lead vessel, large enough to sub-

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[1] "Zeller die künstlichen Kohlen," Berlin, 1903.

[2] *Z. angew. Chemie*, **1903**, p. 195.

[3] Dammer, **1**, 371.

[4] *Z. angew. Chem.*, **1896**, p. 225.

merge the largest pieces to be polished. It is placed directly in front of a ventilating tube, through which a ventilator creates a strong suction. This protects the polisher from the strong vapor given off by the acid mixture and he needs only a rubber apron and long rubber gloves for his protection. The perfectly clean and partly dried off pieces of glassware are held one at a time from $^1/_2$ to 1 minute in the acid, and then immediately dipped into water.

By the action of the acid on the glass a thin crust is formed consisting of calcium fluoride, probably with some sulfate of lead and sodium or potassium fluoride. This is removed by brushing with water, after which the pieces are washed off in clean water and dipped again in the acid. The polish is usually complete after three dippings. Every piece is carefully inspected and defective spots are polished by hand; if the grinding was carefully done, this is rarely necessary.

Experiments undertaken to polish plate glass in the manner described did not produce satisfactory results. The surface obtained was glossy, but in place of being perfectly smooth, as is the case with cut glass, it was somewhat wavy. This difference may be caused by the materially different composition of the two glasses or by the different manner of production.

III—CLEANING BUILDINGS IN INDUSTRIAL DISTRICTS

Buildings and monuments, particularly in industrial districts, obtain in course of time a dark color. This can be removed and the original color restored with hydrofluoric acid better and cheaper than in any other way; 15 per cent acid is generally used (30 per cent is diluted with the same volume of water). The workman wears rubber gloves and proceeds as follows: Two or three sq. ft. of the surface are first moistened with a brush or sponge, then painted with the 15 per cent acid (for large surfaces a whitewash brush can be used). After a minute or two the surface is scrubbed with a stiff brush and rinsed with water. The action on granite or sandstone is negligible; marble is acted on a little more and it is advisable to protect polished surfaces, as they are apt to get dull.

This process has been in use in the Pittsburgh district for about 15 years for monuments in cemeteries and for buildings, which can be made to look like new with very little expense.

IV—CLEANING ROOFS OF GREENHOUSES

The glass roofs of greenhouses are cleaned in a similar manner. During the summer these are usually whitewashed to moderate the rays of the sun. This protective covering, on which also accumulates some dust and soot during the summer, has to be removed in the fall, as during the winter all the sunlight obtainable is needed. This is done by painting the surface of the glass with 15 per cent hydrofluoric acid, using a 6 to 8 in. whitewash brush fastened on a long pole. After a few minutes, when about eight rows have been painted, the acid is washed off with water. In this manner the glass is made as clear and transparent as new, much better than was formerly possible with muriatic or oxalic acid.

If the houses are old and the panes of glass not absolutely tight, the glass in those houses where ferns, smilax and asparagus are raised should be cleaned before the plants are set out, because they sometimes get yellow spots from the fumes of the acid, which penetrate through the crevices even though the fumes are not perceptible to human beings. Other plants are less sensitive and show no ill effects.

None of the four processes described above has been patented, which is very remarkable, particularly in this country where an endless number of valueless processes are protected by patents.

57th Street and A. V. Railway, Pittsburgh

THE NEED OF REVISED CHEMICAL STATISTICS[1]

By Bernhard C. Hesse

The information imparted by statistics is of two kinds. The first deals with domestic production and the second with international exchange of commodities.

The difficulty at the outset is the definition of what should appear in chemical statistics. The classification in Schedule A of our Tariff is one way of settling the question; the classification of our Census Reports is another method but what of those products on the Free List in our Tariff that are undoubtedly of interest to chemists and to chemical industries, and what of those other products and industries contained on our Census Reports dealing with industries other than those classed as chemical? The classification adopted by the Germans as illustrated by the reports in the *Chemiker Zeitung*, 1914, p. 169, and that contained in the Monthly Summary of the Foreign Commerce of the United States, as published by the Department of Commerce, are still other methods of treatment.

Those who compile all our statistics are confronted with the responsibility of completing their task and they have, no doubt, done it very well and in the light of the very best information they can get. If there be any shortcomings affecting us in those statistics we can surely look to ourselves as the cause, in that we have not taken proper steps to designate the kinds of materials which we consider necessary for our commercial and industrial information. Also, in making any requests for changes in those statistics, we must be prepared to give heed to the requirements of others.

It is probably true that none of our present methods of handling our statistics comes so near to satisfying the needs of American chemists and chemical manufacturers as would that adopted by the Germans, and yet their classification would not fully meet our requirements.

Our international statistics, in order more nearly to be of substantial service to the chemical interests of this country, need revision but just what that revision should be I frankly confess I do not know. Neither do I believe that any other *one* man knows but I believe that we all agree that they do not fulfill the purpose.

That being the case, the question first to be considered is the remedy. I suggest that the American Institute of Chemical Engineers take the initiative and with the coöperation of all other chemical organizations in the United States ascertain what articles should be specifically enumerated in our import and export statistics; all organization and trade publications should be invited to participate, and care should be taken that every possible interest, both geographical and industrial, is provided for in such an attempt to get the sense of the chemical industry of this country. As a first approximation of such articles, it might be well to take up those that are specifically enumerated in the Tariff and then to take up those that are enumerated by class or sub-class therein. Care will have to be exercised that on the one hand the classification is not too minutely divided so as to make the work burdensome to the Federal Government and without real clarity to those who use the results, and on the other hand, that the classification be not so broad that the user cannot tell with reasonable accuracy what articles are really included in such classifications. No doubt, the German classification will be an excellent guide, but, in making the final list, the statistical data of other countries, such as Great Britain, France and Austria, should be consulted.

The advantage to be gained by such segregation would be to bring to the attention of domestic chemical manufacturers new domestic needs of chemicals supplied from foreign sources, long before such foreign sources have become successfully entrenched in the business in this country. Such things have happened and they may happen again; the way to prevent their recurrence is something of the kind just suggested.

While it is true that in many of our trade journals such information is published in each issue, yet it is unclassified and not arranged so as to be easy of inspection. Indeed, it would be asking altogether too much to expect our publications to do such

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[1] Presented at the 7th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 2–5, 1914.

work; they publish the news and each individual should dig out his own information.

However, the Federal Government, with its large equipment, can more easily tabulate and classify such material, and print and distribute it better, quicker and cheaper than can any other available agency. It is not to be expected that this additional labor should be performed by the Federal Government without recompense. Probably a moderate subscription fee would be sufficient to cover this added expense and doubtless there would be enough subscribers to such a special compilation to prevent its being a source of serious loss to the Government.

The compilation of import and export statistics is a large task, and changes in it should not be undertaken without thorough consideration. Before requesting any such changes we ourselves should undergo every reasonable labor to ascertain what will better answer our requirements, carefully examine those suggestions and test and re-test them to see that we have made no error, and then submit them to those in charge of the statistical work. Suggestions made after such thorough study will no doubt receive correspondingly serious consideration; without some such serious, thoughtful and well-planned suggestion it is not to be expected that the Federal Government will change its present mode of handling the matter.

What has been said of import and export statistics is true of our production statistics, *i. e.*, our Census Reports, and any changes that we may have to suggest in them should be just as thoroughly and thoughtfully prepared, tested and examined as those in the export and import division.

The need of a change is apparent; just what that change shall be requires the most thoroughgoing coöperation of as many chemists and chemical manufacturers in this country as can possibly be induced to coöperate; the initiation of a work of such magnitude is not to be taken up lightly but should be carefully studied, and if positive action be decided upon, all who partake in it must be prepared to sacrifice much time, much thought and much labor.

90 William Street, New York City

THE WAR AND OUR CHEMICAL INDUSTRIES[1]

The Northeastern Section of the American Chemical Society devoted its first regular meeting of the 1914–1915 season, on October 16th, at the Engineers' Club, Boston, to a symposium on "The Effect of the European War on the Chemical Industries of the United States." The speakers were as follows:

J. Russel Marble, of J. Russel Marble & Co., Worcester, *President of the Section.*

W. H. Bowker, American Agricultural Chemical Co., Boston.

W. D. Livermore, American Woolen Co., Lawrence.

C. A. West, of the Eastern Drug Company, Boston.

C. H. White, Professor of Metallurgy, Harvard University.

H. J. Wheeler, American Agricultural Chemical Co., Boston.

THE HEAVY CHEMICALS

By J. Russel Marble

Members of the Section:

Our topic is one which is of universal interest and your Executive Committee thought it might be wise for the Section to spend an evening discussing the effect of the European war upon the chemical industry of the United States.

My knowledge of the chemical industries of the United States is confined chiefly to what is known to the trade as "Heavy Chemicals," that is, Soda Ash, Caustic Soda and Bleaching Powder. The Section knows the theory, and the process of manufacture, and the history of the success of this American enterprise much better than I do. The successful introduction into this country of the Solvay Process, some years ago, for treating salt, and the later process for the decomposition of salt by electricity, has practically driven from the American market the importations of most forms of soda and bleaching powder.

If the reports of the destruction of property abroad are anywhere near correct, it must be a fact that the enormous soda plant of the Solvay Brothers in Belgium has been destroyed. It is impossible for France or Germany to export any of these materials, and the English plants are reported to be running at only about one-half of their capacities because the employees have left for the army.

Fortunately for this country, we have enormous deposits of salt, chiefly located in Northern New York State, under the city of Detroit, Michigan, and in Kansas and Louisiana, and we have immense water powers from which electricity can be generated.

The manufacture of various forms of soda has been especially successful in this country during the last twenty years, and the effect of the European war, in my judgment, will call for very large shipments of these chemicals to the Mediterranean, Australia, South Africa and South America, and should lead to the running of the plants in this country to their fullest capacity, so that the immediate effect of the war on the heavy chemical industry will undoubtedly lead to a larger output, and should lead to higher prices and a more profitable business for the American manufacturer.

J. Russel Marble and Company
Worcester

THE AGRICULTURAL INDUSTRIES

By W. H. Bowker

The European war affects the agricultural industries of this country in various ways, some for the better and some for the worse. It has improved our market for foodstuffs, but it has injured our market for many raw products, especially our crop of cotton, of which we export about 60 per cent to Europe.

I am asked to speak more particularly on the effect of the European war on the fertilizer industry. There are 7,000,000 tons of fertilizer consumed in this country annually, of which probably 5,000,000 are what are called complete fertilizers, that is, containing the three essential elements of plant nutrition—nitrogen, phosphorus and potash. Broadly speaking, plants consume these three essential ingredients in about the following proportions: 1 Phosphorus; 2 Nitrogen; 3 Potash. Thus potash is a very important element of plant food, and, therefore, of complete fertilizers.

Germany, at the present time, controls the sole commercial source of soluble potash. Until recently there have been no similar deposits discovered in the world. Lately, however, similar deposits have been discovered in Spain. If they prove to be as rich and as soluble and as accessible, and it is believed they are, they will compete with the German deposits.

The potash industry has been one of the most profitable in the world. It is said that muriate of potash, the standard grade (50 per cent K_2O), can be mined and delivered at the seaboard of this country for $15 a ton and show a handsome profit. I am told that it was stated in debate in the Reichstag in 1910 that the best mines in Germany could mine the mineral and refine it for about $8 a ton. The price in cargo lots is from $33 to $34 per ton delivered at seaboard. Through the German Kali Syndicate the production of the mines is limited by allotment and the price arbitrarily fixed. It is stated that there have

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[1] We are indebted to Mr. Hermann C. Lythgoe, Treasurer of the Northeastern Section of the A. C. S., for the collection and transmission of the articles included in this symposium.

been more than a hundred well equipped mines, with a capacity equal to six times the world's consumption.[1]

The Government is largely interested in the mines, as are also the nobility, and ruling families of Germany. Thus they are able to limit the output and maintain prices. If need be they can pass laws to nullify contracts, as they did in 1910 when the American buyers had made contracts six months previous in good faith, at $20 a ton. Six months later these contracts were practically nullified by the Reichstag which passed an *ex post facto* law, mposing a surtax of $20 a ton. This we did not regard as fair. I doubt if it would have stood in an international court.

Broadly speaking, American agriculture can do without potash for a time. Little if any potash is used in the great Middle West where the cereals are grown. The great bulk of complete fertilizers is used in the middle and eastern Atlantic states on staple crops such as cotton, potatoes, corn, tobacco, fruits and vegetables. Where we have used fertilizers rich in potash in the eastern states, or where we are practicing intelligent rotation, also plowing in green crops, we can get along for a time with less potash, and in some cases with no potash, depending upon the amount which is left over in the soil, and also upon that which becomes available by weathering.

Prof. Charles D. Woods, Director of the Maine Experiment Station, has recently issued a statement to the effect that the potato soils of Maine, especially in Aroostook County, contain sufficient potential potash to produce an average of 300 bushels of potatoes a year for nearly a hundred years, estimating that a bushel of potatoes requires about one-third of a pound of potash. Through natural agencies a certain small percentage of the soil potash is rendered available every year; nevertheless to produce the great crops in Aroostook County they use from 100 to 200 pounds of potash (K_2O) to the acre. What is not required for the current potato crop is left in the soil for crops which follow in rotation, such as oats, mixed grasses and clover.

In the cereal belt of the Middle West they are growing cereals at the expense of the soil; thus in the wheat belt they produce on the average about 14 bushels of wheat to the acre as against 40 bushels in Germany; 100 bushels of potatoes as against 300 to 500 bushels to the acre in Germany, and 300 bushels in Aroostook County, Maine.

In my opinion the Germans are the best farmers in the world. One of my oldest friends and best teachers was a German chemist, the late Dr. Charles A. Goessmann, who for many years was the Director of the Massachusetts Experiment Station at Amherst. I have the greatest admiration for the German scientists. They are masters of whatever they undertake. They are specialized in the highest degree.

Speaking of the German farmers and German agriculture, do you realize that Germany produces 88 per cent of her foodstuffs? She, no doubt, was well provisioned for this war, and since the women and children largely carry on the actual farm operations in Germany, she will no doubt be able to produce 80 to 90 per cent of her foodstuffs the coming year. Moreover, she has a great asset in her soil. She believes in making a fertile soil still more fertile. A fertile soil in Germany is not one which will produce crops without added fertility, but one to which they add more fertility and still more and by good seed and very thorough culture they are enabled to raise three and four times as much per acre as we do in the United States. The only farmers in America who follow the German system are the market gardeners around our great cities. They keep enriching their soils and thus they are able to produce large crops in normal seasons, and in abnormal seasons their crops are less injured by drouth, plant diseases and pests, for a well-fed crop like a well-fed man will better withstand abnormal conditions.

According to statistics published by the Department of the Interior, United States Geological Survey, Summary for 1913, pages 103 and 104, we imported into this country potash salts for that year as follows:

		Equivalent net tons K_2O	Basis Per cent
Kainit	465,336 long tons of *2240 lbs*..........	62,541	12
Manure salts	223,687 long tons of *2240 lbs*..........	50,106	20
Chloride of potash	475,261,595 lbs	118,815	50
Sulfate of potash	88,698,193 lbs.......................	21,288	48
	Total,	252,750	

This is equivalent to 505,500 tons of muriate of potash, the standard grade imported; of this it is estimated that from 280,000 to 300,000 tons are used in fertilizers. The remainder is used in the arts, but more particularly in the manufacture of black powder.

Will Germany let out her potash in time of war? If she dared to do it she undoubtedly would, because it is a great source of income, but, as you chemists know, potash is the basis of many explosives and as it might fall into the hands of her enemies and be used against her she is likely to place an embargo on it; but as soon as the war is over it will come forward freely.[1]

Have we any sources of potash in this country that are worth considering at this time? As I have stated, our annual consumption of potash is about 500,000 tons. At Searles Lake, California, according to government estimates, there is a natural deposit equivalent to about 600,000 tons, or about one year's supply. A trial plant is about ready, having a capacity of about five tons daily or for 1915 say 1,500 tons. In Oklahoma there is a possible source of sulfate of potash; in Texas results seem to indicate the presence of potash about 2,200 feet below the surface. Alunite, yielding after treatment about 18 per cent sulfate of potash, exists in Utah, Colorado, Nevada and Arizona. The great source of potash in this part of the country is the feldspar and granite rocks of New England. Many of them, as you know, contain from eight to twelve per cent of potash, but as yet no commercial process has been perfected for rendering this potash quickly available to plants.

There is a great fortune awaiting the man who can invent a feasible and cheap process, but the potash must be rendered soluble in water, and it should be produced at a cost not exceeding $20 a ton (on the basis of muriate) laid down in the eastern markets, for if put to it the Germans could sell their potash at that price in this market, and even for less. So if any of you chemists have a process up your sleeve don't waste any time over it unless you can produce water-soluble potash to compete with the German source.

Now one word as to a substitute for potash. It has been claimed, and some experiments would seem to substantiate the claim, that certain crops, in the absence of potash, will substitute soda. These crops, however, are not the great staple crops like corn, potatoes, cotton, etc. Where this substitution has taken place, it has been with crops which belong to the root family. It is believed, however, that the use of available phosphates will help many crops to assimilate potash from the soil.

At a recent meeting at Mount Carmel Experiment Farm in Connecticut, Dr. Jenkins, Director of the Connecticut Experiment Station, spoke as follows:

"My opinion is that, in our general farm practice, it will pay

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[1] Since the above statement was made there has appeared in the "Country Gentleman" of October 24, an article entitled "The Fertilizer Situation" in which Prof. H. A. Huston, who takes care of the Kali Propaganda for the eastern and southern states, is quoted as saying: "We have 190 mines, 40 of which would supply the world very nicely. We are prepared for almost any sort of emergency demand." The article also states "that the Syndicate is spending a million dollars a year in its world-wide campaign, about one-fourth of that sum in the United States, and any farmer who cares to study the statistics showing the enormously increased use of potash in American fertilizers during the past decade must be convinced that advertising pays."

[1] Since the above statement was made it is reported in the papers that Germany has raised the embargo on 1,000 tons *via* Rotterdam, in exchange for cotton.

better to use available phosphates more freely and potash, in many cases, less freely than we are doing.

"I do not believe in the use of ground phosphates on our thin soils, deficient in humus, but let us stock up our land with available phosphates which we can get, in place of potash which we cannot get, and we may perhaps find a benefit to our farming from this 'war measure.'

"Do not understand me to argue against the need and the use of a liberal amount of potash in our fertilizers. I am merely stating my conviction that, on land where potash has been freely used in the past, a one year's lack of it will not seriously reduce the general crop production of the state, particularly if we will make increased use of available phosphate."

These, however, are technical questions which Dr. Wheeler, who is present and was formerly Director of the Rhode Island Experiment Station, is better able to discuss than I am.

In closing let me say there is no fear of American agriculture breaking down this year because we cannot get potash. There is no fear of its breaking down in the Middle West for some time, if we do not get potash; but the South and East, unless we have potash within two or three years, will be put to it to raise their staple crops. Let us hope that before that time arrives we shall have plenty of potash from other sources to compete with the great German deposits.

The American Agricultural Chemical Company
Boston

THE TEXTILE INDUSTRY

By W. D. Livermore

I cannot add anything to the knowledge of those present who are personally connected with the textile industry, but I shall try to speak in a general way, and in respect to the woolen or worsted industry only.

The first effect was felt in the fear of scarcity of money with resulting fear, cancellation of orders, trade failures, etc., which might even lead to shutdowns in the textile industry.

This phase, as the real situation developed quickly, passed and was followed immediately by some confidence that the business end of the textile industry in the woolen branch might not be injured at all by the war. About this time our anxieties regarding supplies that had usually been imported began to rise, and have not by any means been removed yet. This feature is, of course, the one that appeals most sharply to mill chemists, purchasing agents, etc. The chemist who had planned a nice vacation realized a chance to cancel it and an astonishing change of spirit came over us in our relations with our friends in the dyestuff business. We used to let them come to see us and were quite careful and even critical regarding just what brands of colors we could best use and what we ought to pay for them. In the twinkling of an eye we experienced an undreamed of change of heart.

The dealer whom we suspected of having a good stock of anything we thought we could use became dearer than a brother; we rushed out to see him about it, we wrote him and we called him frequently on the telephone and told him what a lot of business he had always done with us. And I may say that he treated us kindly—he didn't remind us of all the knocks we had given his colors in the past, and he had the opportunity of a lifetime to work off the second best colors he had had on hand for a nice long time. We took them gladly and besought him to find us some more.

Seriously, however, I suppose that the mills of this country are far more frightened than really hurt, but what the future holds we can hardly predict.

We hear very many stories of four and five times the normal price being paid freely for dyestuffs and chemicals and no doubt these stories have a basis of fact—nevertheless, I think they are largely comparable to the case of the wealthy party who pays $40.00 for a pair of $2.00 seats to the Yale-Harvard Football game. Undoubtedly he pays it, but he sits along with some 30,000 people who paid $2.00 each and who do not receive special mention in the newspapers.

If colors are going to come to us *via* Denmark, Holland and Italy, as we hope with considerable reason, we may be troubled with nothing worse than a moderate increase in cost and a necessity for carefully looking ahead and getting our supplies for a period further in advance than has been our custom, and for avoidance of exceptional dyestuffs which are not staple even in ordinary conditions.

The consumption of the United States is in the neighborhood of 15 per cent of the total production of dyestuffs in Germany.

If we can get from Germany 15 per cent of their normal annual production we can take care of ourselves quite comfortably. In support of a hope that we can do this it is easy to remember that Germany will not export any color or raw material for color in such a way that it can be obtained by the countries now hostile and that these countries include practically all the important textile producers outside Germany, Austria and Italy, and also that Austria and Germany are likely to be much too busy with the war to use their full normal amounts of color themselves. The normal stock of colors produced in advance of requirement will, therefore, last us quite a long time if we can get it over here.

As to present production in Germany I do not believe we have very reliable information. I have heard statements running from a present production of 40 per cent of normal in some places down to the closing of the factory and its use as a hospital in others.

It is also worth notice that those organic raw materials which can be converted into high explosives and other war material will be so used and wholly removed from consideration as far as our affairs go.

Some color will be obtainable from Switzerland. England, which usually furnishes a modest percentage of our supply, has practically dropped out of our market—they themselves need more than they have.

Should the worst happen and Germany be entirely closed to us by the course of war, some of the older wood colors like Logwood, Fustic and the Tannins will have a sustained boom. Whether these will be enough to go around will then be an interesting question, but I do not think we want to cross this bridge till we get to it.

As for the proposals for development of our own dyestuff manufactories I think something helpful will be done—but that it will in any very large way fill the gap I can see no great probability. It takes too large an investment, too much technical skill and experience, and even more important, too long a time.

As for the textile industry itself, and apart from this consideration of supplies, it is worth while to remember that no large amount of cloth is likely to be imported for some time—certainly not in the quantities which many of us feared as a result of the new tariff and in this way at least we ought to benefit.

For the first time in the experience of some of us we have heard talk of large orders of blankets and cloth, etc., from abroad. It may be talk only but at least it is very encouraging to those of us who think this means that we shall at any rate have the opportunity to supply our own people with their textiles for the present and that our severest competitors will be among our own manufacturers.

American Woolen Company
Lawrence, Mass.

THE DRUG TRADE

By C. A. West

I wish to speak, not on the trade of dyestuffs or chemicals used in the textile industries, but more particularly on the chemicals used in the arts and in the manufacture of medicines, and I think the general opinion is that there never was such an opportunity for American chemists as presents itself at the present time. The fluctuations in the market during the last month have been greater than ever known before, and we are very much in the position described by Mr. Livermore—that of people willing to buy what medicines they can get.

You may be interested in a few items which I have jotted down. The normal price of benzoic acid is 22 cents per lb.; the price reached $1.25 and went up to $1.50. Carbolic acid which cost us 14 cents per lb., we could have replaced at $7^1/_2$ cents per lb. and we figured a loss of $20 a drum; we sold most of it for 40 to 50 cents per lb. Citric acid which was sold freely at 54 cents (at which we make an average profit of a cent a pound) went as high as $1.35 per lb. One of the large manufacturers came into our store and wanted five kegs of citric acid. We told him the price would be $1.25. Then he wanted to know how much we would charge him for 5 kegs more. We told him $1.30. Then he wanted to know how much we would charge him for 5 kegs more and we told him $1.35. For 5 kegs more, he inquired, and we told him $1.40. "Well," he said, "I guess we had better wait a little while and see what is doing."

Oxalic acid went from $7^1/_4$ to 22 cents, salicylic acid from 25 cents to $1.25, tartaric acid from 30 to 75 cents, arsenic from $2^3/_4$ to 6, nitrate of barium from 5 to 15, calomel from 60 to 90, camphor from 45 cents to $1.00, carbon tetrachloride from 7 to 15 cents, cream of tartar from $23^3/_4$ to 60, Epsom salts from 1 to 3, chlorate of potash from $7^1/_2$ to 25, potassium permanganate from 9 to 60, saltpeter from $4^1/_2$ to 12, quicksilver from $36 to $100 and back to $55, and oxide of zinc from $7^1/_2$ to 25 cents. So I might go on mentioning many others.

When I was in London the last of August I saw an order from the U. S. for Hydroquinone at $3.00 a pound, the price of which today is five times that. Such extreme prices, however, cannot be maintained for the simple reason that everybody in the country who had a surplus stock dumped it into Boston or New York for sale at the best price obtainable. But when you consider or stop to think of how this war is going to benefit American chemists I believe it will be a great gain if they only rise to the occasion.

EASTERN DRUG COMPANY, BOSTON

INFLUENCE OF THE EUROPEAN WAR ON THE METAL INDUSTRIES

By C. H. WHITE

An inspection of the accompanying charts will show that at the outbreak of the war the prices of all the more important industrial metals rose, except pig-iron, copper, lead, and nickel.

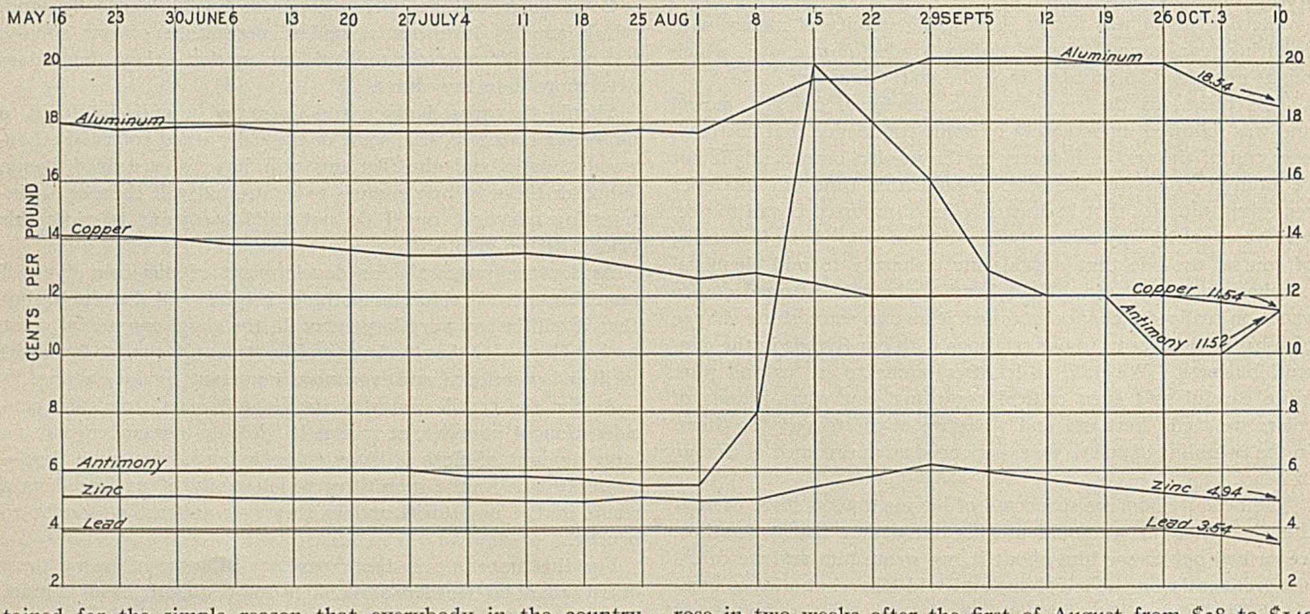
Less than one-twentieth of our pig-iron is produced from imported ores. Of this about $4,000,000 worth comes from Cuba and half as much from Sweden. The war, therefore, can produce no shortage in ore; it creates almost no demand for iron; and, on the other hand, depresses business in general to such an extent that the demand for iron has grown less and less. The producers are unwilling to reduce the price to a figure lower than $14 per ton, the price at which it has been held for many months, and as the demand decreases, prefer to reduce the supply by blowing out their furnaces. Seven furnaces were put out of operation during September.

About half the copper produced in this country is exported; those countries now at war usually take most of our export. The producers have been curtailing the output, but the reduction has not reached the point of holding up the price which can hardly go much lower than it is at present, $11^1/_2$ cents. A lower price would close many mines and this would so check production that the price would gradually go up again.

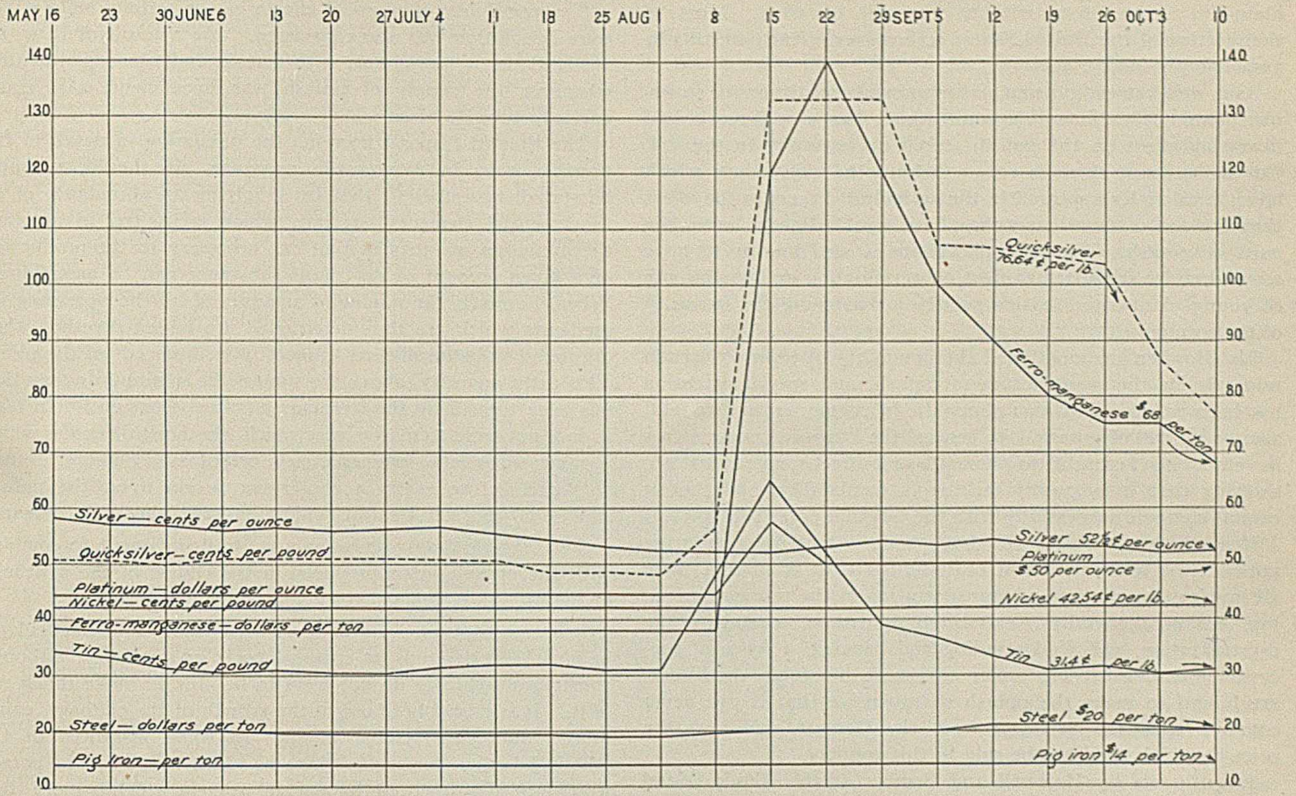
Our exports and imports of lead are about equally balanced. The imports come chiefly from Mexico, South America, and Canada. The war does not interfere with the imports and there is therefore a tendency towards the accumulation of lead, which has lowered the price from 3.9 cents, which it has maintained for many months, to 3.5 cents.

A considerable quantity of our nickel is derived from blister copper, but our chief supply comes from Canadian ores. About half the production is usually exported and the exports are no doubt seriously disturbed, but the International Nickel Company, having a monopoly, will probably maintain the price at 40 to 45 cents, which has held for a long time.

Of the metallic products which have risen in price, the most conspicuous is ferro-manganese. The price of ferro-manganese rose in two weeks after the first of August from $38 to $140 per ton. Ferro-manganese comes chiefly from England and Germany, and three-quarters of the ore from which we make ferro-manganese in this country comes from British India, Brazil, Russia, and Germany. The steel-makers were naturally afraid their supply would be cut off, and, therefore, bid up the price. This advance in the price of alloys used in steel-making, together with diminished business, increased the cost of steel. It advanced from $19 on August 1st to $21 on September 12th, but declined again to $20 on October 10th.



We are not dependent upon Germany for manganese. It was found also that certain cargoes of manganese ore from India consigned to Germany were diverted to the United States.



The price of ferro-manganese dropped in four weeks from $140 to $80, and was down last week to $68 per ton.

The war has created a demand for special forms of steel. England, I believe, has ordered 125,000 tons of sheet bars, the sheets to be used for winter barracks. The wire mills are running at 80 per cent capacity to supply barb wire for the foreign demand, and Russia, I understand, has bought all the wire cutters that could be found on the market in this country.

Our importation of tin amounts to more than $50,000,000 worth annually. The ore comes chiefly from the Malay States and Bolivia and the metal is reduced from its ores abroad. The fear of interruption of the supply put up the price from 31 cents to 65 cents per lb., but it gradually fell back to the former price of 31 cents when confidence was restored in England's supremacy at sea.

A long war should lead to the reduction of the ore in this country, especially the ores from Bolivia.

The price of zinc advanced in three weeks from 5 cents to 6¼ cents per lb., but has since declined to 4.9 cents. Because Belgium and Germany are large producers of zinc, a war involving those countries would naturally create a fear of scarcity of that metal. The United States, however, produces about as much as it consumes, and there is, therefore, no cause for alarm here. England's excess consumption over her production has been about equaled by Belgium's excess production over her consumption. It is probable that, if the war continues long, England will turn to us for zinc.

About one-third of the antimonial lead produced in this country comes in crude form from other countries. In addition to this, considerable quantities of type metal are imported. Under these conditions, war would naturally put up the price. The same is true of platinum and bismuth, which are scarcely produced in this country at all.

One-eighth of the aluminum ore treated in this country is imported, and about one-fifteenth of the metal produced is exported. We, therefore, consume a little more aluminum than our mines produce. The rise in price from about 18 cents to a little more than 20 cents per lb. indicates that there was fear of a slight shortage, but the price has recently fallen back to 18.5 cents.

We produce upwards of $1,000,000 worth of quicksilver, but to supply the demand for home consumption our imports have to exceed our exports by about $30,000 worth. The war created a demand for fulminate which put the price up from $36 to $100 per flask of 75 lbs., but, since the first scare has subsided, it has dropped again to about $60 a flask.

If the war is short, the metal industries should soon become normal again. If it is long, there will probably be still further curtailment in the production of iron and of steel, except in certain forms, and of copper and lead, but I think further declines in the prices will be small. In addition, if war continues we should expect an increase in the production of ferro-alloys and tin in this country.

Department of Metallurgy
Harvard University, Cambridge

DISCUSSION

By H. J. Wheeler

In the course of Mr. Bowker's remarks, he mentioned the fact that "Little, if any, potash is used in the great Middle West where the cereals are grown."

In order to emphasize more fully the significance of this point I should call attention to the fact that it is but rarely that more than from 150 to 300 lbs. of fertilizer are used to the acre in the Middle West and Southwest for wheat and corn crops. The amount of potash in these goods usually ranges from 1 to 4 per cent, although 2 per cent would probably represent fully the average for those sections. This would mean that from 3 to 12 lbs. of potash is the usual amount applied to the acre, while the average application would probably be about 6 lbs.

It must be evident, therefore, that the soils of that section of the country contain enough available potash to produce quite abundant crops, even without the aid of more. Most of that section of the United States is, however, greatly lacking in available phosphoric acid.

As is well known, gypsum is a prominent constituent of superphosphate. This is a substance which has a well-recognized liberating effect on the potash stored up naturally in the soil. On this account there is reason behind the suggestions which have occasionally appeared in the agricultural press to the effect that the use of more superphosphate would slightly lessen the need of potash. The superphosphate is also known to have a wonderfully stimulating effect on germination and the growth of young plants, and it aids greatly in hastening the maturity of the corn crop.

Mr. Bowker has mentioned the possibility of utilizing certain minerals for the manufacture of potash, and special attention has been called recently to phonolite, in particular, and to feldspar as sources of potash. In general the European experiments have not been favorable to phonolite as a direct source of potash, showing that it is greatly lacking in availability, and that it cannot compete successfully with the German potash salts.

Recently several processes have been patented for securing potash from feldspar, but it must be borne in mind that these all involve the mining and transportation of the product, grinding, fusion (generally), extraction, filtration, concentration, crystallization, and final grinding and bagging, a series of processes which, excepting under the most favorable conditions, are bound to make the potash so expensive that it can never compete with the products from the German mines at the price at which they can be sold in this country.

Experiments by Hartwell and Pember at the Rhode Island Experiment Station covering two seasons, and conducted under optimum conditions as far as the moisture content of the soil was concerned, failed to show any particular value of finely ground feldspar as a direct source of potash for plants, whereas the German potash salts gave excellent results. It should be stated that the feldspar which they used was ground so finely that all of it would pass a sieve having 200 meshes to the linear inch.

These results, therefore, utterly dissipate the faint hope of the direct economic utilization of feldspar for agricultural purposes which was held out by Cushman a few years ago.

Another point, touched upon by Mr. Bowker, was the possibility of the substitution of soda for potash in plant nutrition. In regard to this matter, it has been established beyond question by various investigators that soda cannot entirely replace the potash. Nevertheless, it is true that certain classes of plants will take up much more potash than they require, if it is present in readily available form and in excessive quantities. Under such conditions, if available soda is present, it is substituted for some of the potash with no apparent disadvantage to the plant, and at the same time the available potash of the soil is conserved.

The question of the effect of soda in connection with the growth of plants has been studied continuously at the Rhode Island Experiment Station from 1894 until the present time. Crops have been grown in the field, in pots, and also in solutions. In this last case the possibility of any indirect or liberating action of sodium salts on potassium compounds was eliminated. The possibility of physical effects of the sodium salts which were in solution was also considered. As a result of these investigations, it was shown with cereals and other plants that whenever the supply of potash was insufficient, soda could partially take its place.

The time at disposal prevents the discussion in detail of the possible ways in which soda may act. It should, perhaps, be stated, nevertheless, that by supplying an abundance of all the essential elements but one, which is limited in amount, the minimum quantity of that one necessary to the production of a given amount of dry plant substance can be ascertained. When, however, the minimum amounts of all the necessary ingredients which are thus determined are added together, they are found to be insufficient to meet fully the needs of the plant. This extra quantity, above the sum of the minimum necessities, has been termed by the Germans as "Luxusconsum." In fact, it does not seem to matter very much whether this excess which is taken up is lime, magnesia, soda or potash. Soda, therefore, as stated before, exerts a conserving action upon the potash supply of the soil by thus aiding in satisfying this demand.

Soda also doubtless serves as a neutralizing agent to combine with the organic acids produced in the course of the synthesis of the protein compounds of plants.

It is true that sodium salts have been found to be particularly helpful to such crops as turnips, beets and radishes, although spinach and chicory do not seem to be able to make much use of it. It is probably of use in the growth of the cabbage, cauliflower and other related plants. In some instances in the Rhode Island experiments where as much as 40 lbs. of potash were applied to the acre for mangel wurzels, which is more than six times the average amount used for the cereals in the Middle West, it was found that the application of considerable quantities of either common salt or soda ash usually greatly increased or doubled the crops.

This question of the action of sodium salts has not only been studied by Hartwell, Pember, Brazeale and the speaker at the Rhode Island Agricultural Experiment Station, but it has also been studied extensively in Europe by Hellriegel, Wilfarth, Wimmer and their co-workers and successors at the Agricultural Experiment Station at Bernburg, Germany. Many of these results have been published in the "Hefts" of the "Deutsche Landwirtschafts-Gesellschaft."

Some exceedingly interesting results in the same line are reported by Wagner and Dorsch of the agricultural experiment station at Darmstadt, Germany. Smets and Schreiber in Belgium have also shown that sodium salts are of great benefit to plants under certain conditions of field culture.

In a tabulation ("Der Chillisalpeter") of the results of experiments in Europe with nitrate of soda and sulfate of ammonia, Stutzer has shown that for beets and certain root crops, nitrate of soda frequently gave better results than sulfate of ammonia, whereas the reverse was sometimes true in connection with cereals. This, therefore, coincides with the previous reference to the fact that the beet, turnip, radish, and a few related plants can make a greater use of soda than cereals, millet, and other similar plants.

THE AMERICAN AGRICULTURAL CHEMICAL COMPANY, BOSTON

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The Seventh Annual Meeting of the Institute was held in Philadelphia, December 2–5, 1914. The headquarters of the convention were at the Hotel Adelphia and the technical meetings were held in the large lecture hall of the Franklin Institute. The arrangements for the meeting were in charge of the local committee consisting of the members of the Institute residing in Philadelphia, with Dr. S. S. Sadtler as chairman. Great credit is due to this committee for the carefully prepared program of both papers and excursions, which insured for them the large attendance of delegates representing almost every industry and every industrial center.

The first business session convened at the Hotel Adelphia, and the delegates were welcomed by Mr. W. C. Cattell on behalf of Mayor Blankenburg and the city administration. At the business session which followed, the results of the election of officers for the coming year were announced. Dr. George D. Rosengarten of Philadelphia was elected President. Dr. Rosengarten is a graduate of the University of Pennsylvania, class of 1890. Subsequent to graduation, he traveled extensively abroad and studied for his doctorate in Jena. In 1901 he became Vice-President of the firm of Rosengarten & Son, Inc., and took charge of the technical research and manufacture of the various products produced by that company. In 1905 he became Vice-President of the consolidated company of Powers, Weightman and Rosengarten.

Prof. John M. Stillman, of Los Angeles, was elected Vice-President; Dr. John C. Olsen, of New York City, Secretary; Dr. F. W. Frerichs, of St. Louis, Treasurer; and Prof. A. W. Smith, of Cleveland, Auditor; Thomas Griswold, George C. Adamson, J. B. F. Herreshoff and Samuel P. Sadtler were elected Directors.

After the election of officers the business session was devoted to the presentation and discussion of the reports of the officers and the various standing committees.

SOCIAL FEATURES

The Institute banquet, the principal social feature of the meeting, was held in the Green Room of the Hotel Adelphia. Dr. Chas. F. McKenna presided as toastmaster. Mr. W. C. Cattell responded to the toast of the City of Philadelphia, and gave a most charming and instructive talk on the influence of Philadelphia as an industrial center. Mr. M. C. Whitaker, Retiring President, spoke on our industrial outlook and the responsibilities of the Chemical Engineer to avail himself of the opportunities which are presented by the foreign complications. Dr. George D. Rosengarten, the President-elect of the Institute, spoke of the plans for the coming year, and referred especially to the coming semi-annual meeting, which is to be held in San Francisco in conjunction with the other chemical and engineering societies. Dr. Rosengarten was followed by Dr. Wm. H. Bower, First Vice-President of the Henry Bower Chemical Company, who spoke appreciatively of the work of Dr. Rosengarten, and the future prosperity of the Institute. Prof. A. W. Smith, Director of the Chemical Laboratory of Case School of Applied Science, Cleveland, spoke for the western delegation, and extended a cordial invitation to the Institute to hold its next annual meeting in Cleveland, and Dr. H. S. Miner, Chief Chemist of the Welsbach Company, spoke encouragingly of the activity of the American Chemical Engineers in meeting the great problems forced upon us by the European crisis.

Dr. George D. Rosengarten, President-Elect, American Institute of Chemical Engineers

PAPERS

The Manufacture and Application of the Artificial Zeolites in Water Softening. By D. D. Jackson. The speaker discussed the scientific principles involved in the operation of the artificial zeolites in the reversible reactions utilized for the removal of insoluble-soap-forming substances from water to be used for industrial purposes. The process of manufacture of the artificial zeolites was fully explained and illustrated by experiments. Cobalt and manganese zeolites, which have been developed for certain catalytic operations such as the oxidation and removal of chlorine from certain sterilized waters, were discussed. The speaker illustrated with lantern slides the arrangement and equipment of the recently completed American plant for manufacturing artificial zeolites and showed samples of the products at the various stages of the manufacturing process. This was followed by illustrations of working installations of the filtration plants and quantitative figures were presented showing operation results, costs, etc. The paper proved to be of great interest to the members and brought out considerable discussion.

Feldspar as a Possible Source of American Potash. By Allerton S. Cushman and George W. Coggeshall. This paper was presented by Dr. Cushman and embodied a discussion of the various problems—scientific, commercial, political and international—involved in the production of potash from the large feldspar deposits of the Atlantic states. Considerable discussion followed.

Distribution of Industrial Opportunities. By George Otis Smith, Director of the United States Geological Survey. Director Smith presented the principal address of the Philadelphia meeting. He optimistically indicated the direction for industrial development in America, and referred to many of the great problems of natural development which now await the attention of American Chemical Engineers. This address is herewith printed in full.

The Chemical Industries of Japan. By Jokichi Takamine. Dr. Takamine has recently returned from a trip to Japan and gave the institute a résumé of his observations of the chemical industries of that country. His lecture was amply illustrated with lantern slides and conveyed a clear and instructive impression of the industrial problems of Japan and the skill and thoroughness with which they are being developed. At the conclusion of his formal talk, Dr. Takamine was induced to show a number of colored slides illustrating the beautiful landscapes and many of the domestic and social customs and conditions of Japan.

Hydrometallurgical Apparatus and Its Use in Chemical

American Institute of Chemical Engineers at the Welsbach Plant, Gloucester, New Jersey

Engineering. By John V. N. Dorr. Mr. Dorr discussed the possibility of applying the apparatus developed for continuous operation hydrometallurgy to the various chemical industries in which large quantities of material are handled. He illustrated the application of classifiers, thickeners and agitators to a variety of problems and elaborated particularly on the possibilities of the adoption of the principles of continuous counter-current decantation as a substitute for intermittent filtration. Mr. Dorr's lecture was illustrated by a large number of lantern slides showing the details of construction of the apparatus under discussion and also a large number of working installations. The costs of handling both the materials and products were also carefully discussed.

Hardwood Distillation Industry. By E. H. French and James R. Withrow. This paper was presented by Mr. French and is published in full elsewhere in this issue. A large number of lantern slides of working installations were shown and described by Dr. Withrow.

Need of Up-to-date Manufacturing Statistics. By Bernhard C. Hesse. Dr. Hesse called attention to the fact that we are in serious need of up-to-date statistics in regard to the domestic manufacture and importations. These statistics are not now forthcoming from the Government Statistical Bureaus, but we are entirely dependent upon foreign sources for such information as we are able to obtain. He urged upon the chemical engineers the desirability of dependable statistics of the right kind, and also that they formulate their needs and present them to the proper federal authorities for their consideration. As a result of Dr. Hesse's address, the Institute authorized the appointment of a committee to coöperate with the other chemical societies and report upon a specific plan for the collection, formulation and presentation of up-to-date industrial statistical matter which is so urgently needed. Dr. Hesse's address appears elsewhere in this issue.

A Study of the Cause of Paint Failure. By G. W. Thompson. Dr. Thompson presented the results of the investigations which he has conducted to establish the cause of paint failure and its possible remedy. The paper was fully illustrated by lantern slides.

The Potash Industry. By H. A. Huston. Dr. Huston discussed with considerable detail the present potash situation and its probable bearing upon the agricultural development of this country. His paper was fully illustrated by lantern slides and these were followed by a most interesting series of moving pictures, showing the operations of the various departments engaged in mining and refining potash salts.

EXCURSIONS

As is customary in the Institute, a large portion of the program was devoted to the inspection of industrial plants. The excursions were unusually well attended and the greatest interest was shown, especially in the more modern engineering developments as applied to the various industrial processes.

Atlantic Refining Co., Point Breeze. The members were here enabled to see the various processes developed for the refining of mid-continent crudes. The ordinary refining process is illustrated by a large number of installations. The Frasch stills were seen in operation, and the Burton process for the manufacture of motor fuel proved to be of great interest.

United Gas Improvement Company, Point Breeze Plant. The delegates had an opportunity to inspect the new water gas generators with the waste heat boiler installations, the physical research laboratory and the recent developments in artificial illlumination and photometric apparatus.

Welsbach Company, Gloucester. The members spent the greater portion of one day in a detailed inspection of the various operations in this plant. The inspection was carefully organized by Mr. Miner and his staff, and the visitors had an opportunity to see the manufacture of nitro-cotton, collodion, thorium nitrate and gas mantles. The plants for the recovery of collodion solvents, camphor, and the recovery and distillation of waste ammonia liquors were also points of interest. The Welsbach Company entertained the guests at luncheon, which was served in the engine room of the metal factory.

The New York Shipbuilding Co. A portion of the delegates visited the plant of the New York Shipbuilding Co., in Camden, and inspected the shops and factories of this large property. A number of large merchant and war ships were seen in process of construction.

Farr and Baily Linoleum Works. A large delegation visited this plant and inspected the process and equipment for the manufacture of both inlaid and printed linoleums. The process was shown from the oxidation of the linseed oil to the finished product and proved to be a most interesting illustration of the modern developments obtaining in this industry.

Commercial Museums. One of the most interesting excursions of the convention was a visit to the Commercial Museum of Philadelphia. The inspection of this unique institution was carried out under the direction of Dr. Wm. P. Wilson, the Director of the Museum, and his corps of assistants. The plan and purpose of the museum was carefully explained to the visiting delegates and the collections proved to be most interesting and instructive.

The visit to the museum was followed by an inspection of the near-by laboratories and plant of the University of Pennsylvania.

Barrett Manufacturing Co. An unusually large number of visitors were the guests of the Barrett Manufacturing Co. where they were shown the working up of the light and middle oils from the various crude refineries of this company. Every operation of this process was shown, from the distillation of the oils to the refining of benzol, toluol, naphthalene, phenol and other products.

DISTRIBUTION OF INDUSTRIAL OPPORTUNITIES

By George Otis Smith

Four constituents enter into the reaction that we term industry. Two of these, brain and brawn, are organic compounds and two are perhaps to be regarded as inorganic—money and material. None of these components is wanting here in the United States, and in fact their abundance affords the best reason for an optimistic outlook upon the present industrial situation. While in nowise overlooking the large importance of labor and engineering skill and capital as factors in the establishment of new enterprises or the expansion of old industries, I wish to address my remarks chiefly to the subject of the distribution of the raw material that is no less essential to a nation's industry.

In the highly differentiated system of production and commerce, the place factor has assumed large influence. The growth of transportation agencies makes the whole world tributary to both producer and consumer, with the result that keen competition tends to localize and specialize production. By way of contrast, think of the industrial conditions of a century ago. Our grandmothers were in a way chemical engineers. Yet to them, for instance, potash presented no international problem, but as soap-makers they utilized that home supply that gave the material its common name. In those days, as a poet has said:

> "Home was a factory, life a trade,
> And Mother a Captain of Industry."

Today facility of transportation has changed all this and industrial opportunities distribute themselves in accord with fairly definite though often complex principles. Of the four constituents of industry, labor, capital and brains are all more easily transported generally than the crude materials upon large tonnages of which the industry must depend. Thus cheap coal will attract manufacturers just as cheap land attracts farmers.

In studying the statistical record for the years since 1880, which is the period of expansion and development of the mineral industry, I have been impressed with the marvelous increase both in output and in efficiency in operation. Such facts have significance as we face the future. For this third of a century just past the growth of the mineral industry can be summed up in the statement that the value of the output has increased nearly seven-fold, while our population has less than doubled. If we compare directly the output per capita of population, the record of increase in the more important mineral products becomes really instructive or even inspiring. Thus in this period of 33 years the consumption of coal per capita has increased from less than a ton and a half to nearly 6 tons—an increase of 337 per cent. Similarly, the production of iron ore increased 357 per cent, petroleum 391 per cent, copper 1200 per cent, cement 2087 per cent; but gold and silver increased only 23 and 22 per cent respectively, while with lead the increase was 125 per cent, and zinc 638 per cent.

If statistics for the more important agricultural products are studied in a similar manner it is found that the total increases in the same period have not much more than kept pace with the growth in population. This is true of the two leading grains, corn and wheat, the one having somewhat more than doubled, the other not quite doubled, in the third of a century, so that the per capita production shows only a small percentage of increase. With cotton the gross increase has been larger, approaching 130 per cent, but wool has utterly failed to increase as rapidly as the population. It is only sugar that shows an increase, both in domestic production and in consumption, at all comparable with that of the half dozen minerals mentioned, the per capita increase being 394 per cent, or about the same as the other carbon compounds, coal and petroleum.

An even more gratifying phase of this mining development is the marked increase in man's productive capacity. Let us take the 20-year period 1889–1909 and analyze the coal-mining record. Roughly stated, the number of mine-workers a little more than doubled in that period, the output of coal more than trebled, and the capital investment more nearly quadrupled. The exact percentages are 123 per cent increase in employees, 226 per cent increase in production, and 252 per cent increase in capital. Stated in terms of efficiency, the mine-worker increased his individual output from 471 to 691 tons a year, while the average annual output per dollar of capital remained nearly the same, about two-fifths of a ton, the increase in capitalization per ton of output being less than 8 per cent. Most of this increase in capital outlay was due to equipment expenditures, the improvement in mechanical equipment appreciably adding to the mine workers' efficiency and comfort.

In iron mining the record for the same period is even more striking; the number of miners increased less than one-half, the capitalization nearly trebled, and the output nearly quadrupled. In the iron mines, then, both labor and capital became more efficient, the output per miner increasing from 385 to 995 tons and the production per dollar of capital from one-seventh to one-sixth of a ton. In the case of coal mining we know that this improvement did not halt with the census year of 1909, for since then the coal output per miner has increased another 71 tons, or more than 10 per cent in the four-year period. All this tells the story of steadily increasing efficiency of mine worker, mine equipment, and mining methods—that is, of the contributions by labor, capital, and engineering.

When I speak of the distribution of raw materials, I do not of course shut my eyes to the influence of markets upon the location of industry. The development of transportation systems makes the problem of markets a most complex one. Cheap transportation may take away a home market from an industry or it may furnish a foreign market. The industrial independence of the small community of a century ago has given way to the system under which your dinner table may represent the tribute from several continents. Even in a country so diversified as ours in its natural bounties domestic production of everything consumed is not desirable nor profitable. Exchange of commodities with foreign countries becomes necessary: for instance, just as soon as America can mine and smelt copper or produce and refine petroleum more cheaply than it can grow tea or raise sheep or cattle, then the home market for cheap meat and wool and tea necessitates a foreign market for our copper and oil.

Of course, the more we as a people are independent of goods sent from other countries the less we are dependent on a foreign market for our own products. Large imports necessitate large exports, else the balance of trade will swing too far on the wrong side. Nor can we shut our eyes to the volume of exports needed to meet the interest obligations due the foreign capital invested in our railroad and industrial securities.

So it follows that in planning industrial development independence is the goal toward which a nation should face, but not a goal which it should have either the intention or the desire to attain. As we look toward the South we find that our commerce with South America for the last four years has been one-sided to the extent of an unfavorable annual trade balance averaging more than $80,000,000. The fact that the balance of trade is against the United States in two of the three "A B C" countries should be taken only as an invitation to export more. That $80,000,000 not only measures the present opportunity for exports to South America but also suggests the chance for further development of trade relations. We need meat and hides from Argentina, tin ore from Bolivia, rubber and coffee from Brazil, nitrate from Chile, platinum from Colombia, cacao from Ecuador, wool from Peru and Uruguay, and coffee from Venezuela—what can we export in exchange?

To increase industrial prosperity this country needs to export finished rather than crude products and to import raw materials rather than manufactures. It is the product of American labor rather than the bounty of our natural resources that preferably should go into the world's markets. Betterment of industrial conditions can come best through expansion of manufacturing. The increase of the element of labor in the product exported will mean that we are not bartering away our heritage of natural resources but rather that we are using these resources as a basis simply for the expenditure of labor, which renews itself.

As the engineers of America study this matter of expansion of manufacturing, it becomes evident that the distribution of raw material and of power is the key to industrial opportunities. So narrow, however, is the usual margin between success and failure that the practical proposition can not be stated in so general terms. The chemical engineer requires not only qualitative but quantitative facts with which to start, and fortunately the geological engineer has come to realize this requirement. What are the mineral resources and where are they?—these are the two questions to be answered by the geologist. The answer to the "what" must be expressed in exact terms, and the value of this or that mineral to industry usually depends upon very specific factors. To illustrate: The knowledge, derived from a study of thousands of rock analyses, that the element potassium constitutes 2.49 per cent of the earth's crust possesses scientific interest and value; but as a starting point for practical work you chemical engineers would prefer a series of a dozen or two analyses of brines and bitterns from Western marshes and Eastern wells; yet even these analyses, however accurate, would avail little except as the geologist would furnish also a quantitative statement regarding the volume represented by such samples—that is, the extent of the deposits available for utilization. And here the scientific statement of relative abundance of potassium in the earth's crust comes in to contribute to the practical work as affording a measure of probability in extent of deposits when discovered.

A source of gratification to the Government scientist, especially in the past few months, has been the fact that under new and special demands many bits of knowledge that had before been only interesting and incidental details in the scientific study of mineral resources suddenly come to possess value recognized and appreciated by the producer and consumer. The dollar mark attached itself to these facts over night.

Already readjustment of domestic industry under present conditions has resulted in the development of American substitutes for imported material. Sales of domestic manganese ores have been made to the glass trade, and production of ferromanganese on the Pacific Coast is reported. The manufacture of zinc dust has followed the shutting off of the foreign supply, and barytes from the South has begun to replace the German imports. Medicinal oils derived from American crude have been placed upon the market by at least two refining companies and advertised as equal in every particular to the Russian article. Several firms have expressed their intention of manufacturing magnesium chloride from California magnesite, of which at least one shipment has been made to the East and others are to follow *via* the Panama Canal. In the Western States an efficient substitute has been found for the Danish flint pebbles used in the tube mills. In California, river pebbles of quartz are used, and in Idaho and Nevada pebbles are manufactured from local rock, and the reports from the mill men are to the effect that these substitutes are giving satisfaction at much lower costs.

In considering fuel and its bearing upon industrial opportunity too much emphasis can hardly be placed upon the distribution of the world's coal. Significant facts are that 98 per cent of the world's production is mined in the northern hemisphere and that of known reserves of coal of all grades the southern hemisphere possesses only $3^1/_2$ per cent. So too, not only does the United States mine and consume 40 per cent of the world's annual output of coal, but this country alone possesses five times as great a tonnage of unmined coal as does the whole of Europe and more than 1500 times as much coal as is known to exist in South America. Do not these facts contain the promise that the manufacturing industry of this country will continue to furnish manufactures for export to Europe and South America in increasing amounts?

When we consider the distribution of coal production and coal reserves, it is noteworthy that coal is mined in 30 states and that over 16 per cent of the area of the United States, not including Alaska, is underlain by coal beds. While Pennsylvania has for a century led in coal mining and thereby possessed a proud leadership in so many industries, this state does not contain the largest reserves. The center of coal production must surely continue to move westward toward the geographic center of the nation's coal reserves, which was figured several years ago as located in southeastern Nebraska—a state, by the way, of low rank both in coal output and coal reserves.

Petroleum and natural gas in their distribution in some degree supplement coal. While the states of the Appalachian and Lima-Indiana petroleum fields are mostly coal-bearing states as well, the largest oil field, both in present production and probable reserve, is in California, a state with only negligible coal resources. Taken together, these mineral fuels constitute a national asset comparable with the soil resources of this country; but the larger part of the value of the natural gas, petroleum, and coal to the nation is in their relation to manufactures.

The wide distribution of the other items in the nation's mineral treasury is no less notable than their abundance. Taking, for instance, the ores of the six important metals, the lack of localization can be seen in the record of last year's production by states. Listing the three leading producers for each of these six metals, we find no less than 13 states, including Alaska, in the competition. Missouri is the only state to rank first for two metals, lead and zinc. Montana stands second in both copper and silver, Colorado ranks second in gold and third in zinc, while Utah stands third in the production of three metals, copper, silver, and lead. These mining districts that are so productive of mineral wealth are scattered over the country from Alaska, ranking third in gold, to Alabama, third in iron ore, and from California, which leads in gold, to New Jersey, second in zinc. Such a wide distribution of ores sufficiently rich and extensive to be mined in large quantities means that the metallurgical industry is important on both the Pacific and the Atlantic seaboards, and in most of the Rocky Mountain states as well as in several of the middle states.

Even in the two metals which at once suggest to us centralization—copper and steel, there is wide-spread production. In the mining of copper last year 23 states contributed, and the mining of iron ore is not confined to any one region, even though the ranges of Minnesota and Michigan furnished 84 per cent of the tonnage and Alabama and Tennessee $8^1/_2$ per cent. In all, no less than 28 states contribute iron ores to the furnaces of the country.

The diversity of the mineral industry is shown by the increase in number of products. Thus, while in 1880 the statistics of production covered 51 products, the table of production in current reports contains no less than 72 items. Furthermore, when the rapid growth of the industry is analyzed the more marked increase is seen in that of the nonmetallic products. The old opinion that the word "mineral" carried the idea of "metallic" is overwhelmed by the relative importance of the nonmetallic mineral products. In 1880 these constituted 47 per cent of the total output; last year more than 63 per cent. Another method of stating this relative importance is to say that the value of the nonmetals last year was greater than that of both metals and nonmetals in any year prior to 1905.

The raw-material resources of this country are so widely distributed that industry has been developing at this rapid pace at many points. I believe the tendency has been away from geographic centralization of industry rather than toward it. The State of Pennsylvania stands in a class by itself as a producer of mineral, yet its preëminence is perhaps less marked each year. Although last year its output was more than one-fourth of that of the whole country, a few years ago its share was more nearly one-third. Other factors are coming to the front each year which will create opportunities in other parts of the United States. You do not need to have these more than suggested: the South with its happy combination of coal and iron-ore in the same districts makes pig-iron production possible at minimum cost; the West with its hydro-electric possibilities available as a source of relatively cheap power for chemical and metallurgical industries; the Rocky Mountain region with its vast unutilized sources of sulfuric acid and equally great unmined stores of phosphate rock.

In these months of rapidly shifting currents of trade we may even see coals carried to Newcastle, but I will not presume to tell industrial chemists anything concerning possibilities of American manufacture of coal-tar products, so essential to other industries. However, it is not apart from the present subject to mention the amount and distribution of raw material available. Of the 115 million gallons of coal tar annually produced in by-product coke ovens, more than 22 millions are available in Alabama alone, nearly as much in Pennsylvania, 16 millions in the Indiana and Illinois region, and nearly half that in western New York. Ohio, West Virginia, Maryland, Kentucky, Wisconsin and Michigan are other important producers. Yet, so far as I am informed, few indeed are the centers where coal tar is used as a basis for chemical industry.

To return for a moment to the industrial reaction mentioned in my introductory sentence—the other ingredients necessary for producing prosperity appear at hand. A financial system already promises more mobile credits. A more sympathetic attitude of the public toward big industrial operations is indicated. The efficiency of American labor and American engineering was never questioned.

Two years ago Mr. William L. Saunders, President of the Ingersoll-Rand Company, gave his fellow mining engineers the benefit of his personal observations on manufacturing in Asia and Europe. His conclusions are of value to all engineers. He stated that manufacturing centers are not determined by abundance of cheap labor; efficient labor and the best tools are the requisites to manufacturing supremacy; *e. g.*, the cheap labor in a Japanese steel works does not yield the low labor items on the cost sheet attained by the American manufacturers with high-priced labor; and finally the real competition with American industry is that of the efficiency of German workmen, reënforced as it is by inventive engineering, rather than that of the cheapness of Asiatic labor.

In any estimate of American ability to make the most of the present opportunities for industrial expansion you can perhaps find no better measure of the inventive genius of this country than in a moment's review of what is making the European war so terrible. Strictly neutral we may be, yet from the heights above to the depths below we find American inventions "at the front"—the aeroplane, the magazine rifle and machine gun, the barbed wire, and the submarine and its torpedo. Can not our nation lead as well in the fashioning of the tools of peace as in designing the machines of war?

U. S. Geological Survey, Washington

CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

4TH ANNUAL REPORT OF THE DIRECTOR OF THE U. S. BUREAU OF MINES

The saving of human life in the mines, the stopping of millions of dollars of waste of mineral resources of the country, and an inventory of the wastes that are continuing are given important consideration in the recently issued fourth annual report of Dr. Joseph A. Holmes, Director of the United States Bureau of Mines.

According to Dr. Holmes, the Bureau has recorded its most notable achievement in the rescue of more than 100 entombed miners at different disasters, and the rescue of many more miners by volunteers who had been trained in life-saving work by the Bureau. Rescue and first-aid stations have been established at hundreds of mines throughout the country. The total number of miners trained by the Bureau has now reached 24,975. Yet, the loss of life is far greater than it should be with the natural hazards of the industry, and a plea is made for more extended investigations on the part of the Government. The humanitarian motives for undertaking such investigations are obvious. A sufficient economic reason is that during the past year more than 3,500 men were killed and more than 100,000 injured in the mining and metallurgical industries of the country. One-half of these fatalities and three-fourths of the injuries may be regarded as easily preventable. The money loss from the accidents may be estimated at not less than $12,000,000 a year, and this loss must be ultimately paid by the consumers of mineral products throughout the country.

The necessity for a more extensive use of safety appliances in the mines is shown by the statement that in the last five years, through lack of such appliances, more than 3,500 men have been killed in the mines and nearly 20,000 seriously injured. In Kansas, Oklahoma, Indiana and Iowa, many of the men employed in the mines to set off the explosives have lost their lives, and the recommendation is made that the shots should be fired electrically from outside the mine. In many districts the methods of shot-firing employed are still so extremely hazardous that only the most reckless men are willing to act as shot firers.

As showing the interest outside the Bureau of Mines in the life-saving campaign in the mines, many of the states are already expending in their work more than the Federal Government in all its investigations in behalf of mine safety; *e. g.*, Pennsylvania expends yearly $213,000. Also, twelve individual mining companies have rescue cars, which is four more than are operated by the Bureau of Mines.

In discussing the causes of mine disasters, Director Holmes says: "Not only have men been killed or injured from what are believed to be unnecessary electrical accidents in mining, but indirectly electrical apparatus has been responsible for mine explosions and mine fires that have extensively destroyed both life and property.

"The improper use of explosives and the use of improper explosives have directly or indirectly caused a large share of the fatal accidents and serious injuries to the men. But fully as serious as the killing or injuring of several thousand men from this cause during the past five years has been the injury to the health of the miners from poisonous gases given off by the improper explosives used.

"Each day poor ventilation and resulting bad air injure the health of thousands of miners. In most of the metal-mining states the statutory provisions are incomplete and inadequate, and there is the greatest disparity between them as to what constitutes sufficient ventilation to keep mine air pure. In fact, no adequate system of ventilation is generally in force today in the metal mines of the country."

During the year, four devices for limiting the area of mine explosions were perfected by George S. Rice, the chief mining engineer of the Bureau, and patented for the benefit of the mining industry. The director considers the development of these devices as probably the most important part of the year's work. The devices consist of barriers placed in the mines and loaded with stone dust. When an explosion strikes these barriers, the stone dust is thrown into the air and stops the further propagation of the explosion.

In the accomplishments of the year, Dr. Holmes calls attention to the statement of his engineers that with an expenditure of $15,000 they have brought about a saving of natural gas worth $15,000,000, a sum many times greater than the total cost of all the work done by the Bureau during the four years of its existence. This was done by introducing better methods in the drilling for petroleum and gas. The waste of gas stopped totaled 350,000,000 cu. ft. per day, equivalent in heating value to 17,000 tons of coal per day. In preventing the escape of this enormous quantity of gas, another saving was made, the value of which cannot be estimated—the elimination of danger to human life from the escape of this gas into the atmosphere. Dr. Holmes estimates the loss to this country each year in the development of the oil fields to be not less than $50,000,000, and that a large part of this loss is preventable. The fact that the principal oil-producing areas of the country are now believed to be well defined, and the fact that the next few years will see a constantly diminishing instead of an increasing production, unite in making imperative the need of extended inquiries.

Attention is called to the discovery of a process by the chemists of the Bureau whereby radium, which is sought much for its supposed curative qualities, can be produced at one-third of its present cost. With radium now selling at $120,000 a gram, its reduction in price to $40,000 will, it is said, result in many hospitals throughout the country being able to purchase a supply. The process devised by the Bureau's chemists has already been tested with success in the plant of the National Radium Institute, which is under the supervision of the technical staff of the Bureau of Mines.

The Bureau also claims that through its scientific method of purchasing coal according to its heat value the Federal Government has saved during the year $200,000 and that the various cities of the country that have taken up this plan of buying coal have reported a saving last year of thousands of dollars. Dr. Holmes places the present waste of mineral resources of the country at the sum of $1,000,000 per day and declares that in a large measure this waste is unnecessary. In one respect at least, the consideration of mineral waste has a basis quite different from the consideration of agricultural wastes. Our crops represent an annual production from a reasonably permanent soil; our forests may grow again, though a much longer period of time is required; and the soils themselves may be reproduced from the subsoil and the rock beneath. But of our mineral resources we have only the one supply. This supply is to a considerable extent destroyed by use, and at the present increasing rate at which we are using and wasting it, our one supply of a number of these resources will be either exhausted or largely depleted while the nation is yet in its youth.

A careful estimate indicates that in the mining of 600,000,000 tons of coal during the last calendar year there was wasted or was left underground in unminable condition 300,000,000 tons of coal. As a result of careful preliminary inquiry, it is believed that more than one-half (200,000,000 tons of coal) of this yearly waste is preventable under existing economic conditions. But the bare statement of the enormous losses does not, perhaps, express the most important part of the situation, which is that the coal we are now using and wasting represents the cream of our supplies, namely, the coal that is the best, is most easily and cheaply mined, and is nearest the great centers of industry.

The annual waste of metals in brass-furnace practice amounts to more than $4,500,000.

A preliminary inquiry as to the coking of coal in beehive ovens has shown that the total value of the by-products annually lost in this country through the use of such ovens amounts to $75,000,000. Although the desirability of developing by-product industries in this country has been recognized, such development has now become an actual need.

BRITISH MANUFACTURE OF ANILINE DYES

Agitation in England for the establishment of a home aniline dye industry is following much the same lines as the same movement on this side of the ocean and the conclusions as to the best means of fostering the growth of such an industry bear in many cases a great similarity to the recommendations made recently by a committee of the New York Section of the American Chemical Society [This Journal, 6 (1914), 972]. In the discussion at a meeting of the Council of the Leeds Chamber of Commerce one of the speakers stated the situation, according to the *J. Gas Lighting*, 128 (1914), 201, as follows: Some form of protection would be necessary for probably the next fifteen years. In Germany the capital sunk in this industry amounts to something like $125,000,000; and their concerns have been built-up gradually during the past 25 or 30 years. They have made a scientific study of all branches of the industry, the raw material for which has come very largely from England. By means of chemical research, they have arrived at the cheapest way of making the intermediate products as well. In Great Britain, on the other hand, the research laboratories have not devoted their attention particularly to the development of aniline dyes, or of the intermediate products which are necessary in the following up of synthetic coloring matters. Thus, the present crisis has found British manufacturers unprepared. Practically 90 per cent of the aniline colors consumed in England were imported from Germany; and the same applies more or less to the whole world. The speaker thought in the circumstances, therefore, that the Government should give some kind of protection for the working of German patents, either on a small royalty, or probably no royalty at all, while the war continued. The customs protection should be from 20 to 25 or even 30 per cent, and should continue long enough to carry the industry over its initial stages.

NICKEL, COPPER AND MERCURY AS AFFECTED BY THE WAR

The world's production of nickel during recent years has been steadily increasing, as shown by the following figures:

	Tons	Tons increase
1910	20,100	....
1911	24,500	4400
1912	28,500	4000
1913	30.000	1500

During the recent six or seven years there has been a remarkable expansion in the industrial uses of metallic nickel. Two-thirds of the world's supply is produced in Canada; the remaining third comes from New Caledonia and is controlled by France [*Engineering* (London), 98 (1914), 614].

A government order was issued in Canada, at the end of October, prohibiting the export of nickel to enemy countries. This contraband of war prohibition will act as an incentive to the opening out of new deposits and re-opening of old ones, several of which are situated in the United States, Greece, and other countries, all well known.

Norway possesses extensive deposits of nickel ore, much of it containing as high as 2 per cent of the metal. In former years nickel-mining was of some importance there, but competition with the richer ores of Canada and of some mines now shut down in the United States, could not be maintained, and most of the mines ceased operation. It is now stated that the mines have been reopened. The Norwegian nickel ore-mining industry was revived on a small scale some years ago, with an annual output of 70 to 100 tons, nearly all of which is used within the kingdom.

In the United States a very limited recovery of nickel is made as a by-product in the electrolytic refining of copper. The U. S. depends practically entirely on the nickel-ore mines of Sudbury, Ontario, for their supplies of the metal. The production of the Sudbury mines during 1913 reached 750,000 tons of ore, most of which was smelted to matte containing about 24,000 tons of nickel. In 1912 the production of these mines amounted to 737,320 tons of ore, while the matte produced 22,421 tons of nickel.

The recent Canadian output and the British imports from the United States are given below:

	Canadian output		Great Britain from U. S. (nickel oxide)	
	Tons	Value	Cwt.	Value
1909	.....	......	19,455	$481,625
1910	.....	......	17,294	430,675
1911	15,222	$10,660,855	15,117	371,550
1912	20,018	14,013,000	23,679	584,870
1913	22,177	15,524,000	17,965	450,600

A portion of the matte made by the Canadian Copper Company is used for the direct production of monel metal, an alloy of nickel and copper, without the intermediate refining of either metal.

The world's production and consumption of copper have been seriously interfered with by the war, and prices are very unreliable, as no one can foresee the probable demand during the immediate future, nor the length of the war. The world's production of copper during recent years has been as follows in tons [*Engineering* (London), 98 (1914), 586]:

Copper Production of the World—1910-1913

1910	891,000	1912	1,018,600
1911	893,800	1913	1,005,900

Copper Production of the World in 1913—Tons

United[States,	589,100	Great Britain	41,000
Mexico	90,000	Russia	34,300
Japan	77,200	Spain	23,600
Australia	41,800	Other lands	56,800
Germany & Austria	52,100	Total	1,005,900

The consumption of copper in several countries is given in the following table:

Copper Consumption in Tons

	1910	1911	1912	1913
England	148,187	159,736	148,877	140,300
France	92,838	106,408	106,753	103,600
Russia	28,237	31,830	38,818	40,200
Germany	208,826	234,985	253,429	259,300
Austria	37,150	41,101	51,574	37,200
Italy	32,487	40,949	34,378	31,200
United States	334,565	316,791	365,922	351,000

Towards the end of September, a noteworthy feature of the copper market was the action of the British Government in acquiring all the stocks of copper carried in Dutch warehouses, as this metal almost always is destined for Germany. Three cargoes of copper afloat for Holland were also taken by the British government.

The copper exported from America, practically all to Europe, during the nine months of the year and the corresponding months in the preceding four years has been as follows (in tons):

	1910	1911	1912	1913	1914
January	26,699	29,357	30,967	24,659	35,566
February	25,238	18,992	35,418	26,767	34,384
March	19,963	23,200	27,074	42,428	46,504
April	31,062	27,466	23,341	33,024	34,787
May	20,832	26,655	32,984	38,251	31,948
June	23,430	30,074	26,547	27,808	35,182
July	22,875	34,955	25,445	29,096	34,145
August	27,876	27,893	29,526	34,722	19,676
September	31,733	25,745	25,572	34,314	16,838

The total American exports for October have been estimated at about 16,200 tons, equal to 36,288,000 lbs.

The total value of the American copper exports may be taken at $146,000,000, of which $128,000,000 represents metal in pigs, ingots, and bars, while nearly all the remainder was exported in plates, sheets, rods, and wire. All these exports come to European countries, with the exception of about $7,098,000 worth, which were sent mainly to Canada. Trade in articles manufactured of copper and brass is comparatively small. The value of European exports of articles manufactured from copper and brass is many times that of the exports of similar goods from the United States.

British exports and imports of copper occur as ore, unwrought bars, blocks, slabs, cakes, and ingots, and copper goods manufactured; the exports and imports of copper ore during recent years have been:

	Copper Ore				Copper, Regulus and Precipitate	
	Exports		Imports		Imports	
	Tons	Value	Tons	Value	Tons	Value
1909	2,333	$220,415	89,153	$4,548,600	65,292	$10,960,785
1910	221	15,930	98,179	4,843,700	68,974	11,327,250
1911	...	....	86,596	4,278,700	64,873	10,037,160
1912	169	4,150	98,226	4,754,300	51,565	10,039,430
1913	...	....	94,265	5,025,300	39,110	7,247,030

Exports of copper ore mined in Britain are on a very limited scale and are practically ceasing as shown by the table. The imports come in small quantities from Germany, Belgium, France and Scandinavia, and in larger quantities from South America. Figures at hand show decreased imports from Chile and increased imports from the Transvaal and Australia.

The above table gives also Britain's imports of copper, regulus and precipitate. They are mainly from Belgium, Portugal, Mexico, Spain, South America, Cape of Good Hope and Australia. The exports are very limited, being last year only 1870 tons, value $19,000.

Great Britain's total copper exports and imports are shown below for the 1909–1913 period.

	Exports		Imports	
	Tons	Value	Tons	Value
1909	40,440	$13,726,500	288,430	$57,846,000
1910	50,210	16,700,000	237,950	46,479,000
1911	50,300	16,870,000	263,740	46,776,500
1912	43,040	14,506,000	251,650	55,146,000
1913	53,200	20,902,000	257,620	56,560,000

Trading interests in quicksilver are attracting attention on account of the very extensive use of mercury in the preparation of fulminate for explosives, the present and probable future consumption of which must have an important bearing on the market for the metal, the withdrawal of available supplies, and the future demand.

Quicksilver is put to many practical uses, such as gold-mining, but probably the most important is for percussion caps for igniting powder. The world's production is increasing; the average for the last decade has been 3728 tons. The output during recent years [*Engineering* (London), 98 (1914), 570] has been as follows, in tons:

1905	1907	1909	1911	1913
3336	3307	3233	3419	4171

The world's supply is obtained from only six countries, the main source being Spain; the Almaden mines of that country produce nearly a third of the entire quantity. Recent outputs have been as follows, in tons:

	1909	1911	1913
Spain	1000	1055	1490
United States	717	742	688
Italy	700	815	888
Austria	609	685	855

Ten years ago the United States' output of quicksilver was the largest in the world, exceeding 1000 tons for several successive years, but since then it has been declining; the main American supply is obtained in California, mostly from one mine. Great Britain's trade in quicksilver is peculiar, in so far as none is produced in the country; it is purchased and distributed, and, in effect, controls the world's markets in the metal. The following schedule shows the imports, exports, and British consumption, in flasks, during recent years:

	Imports	Exports	Consumption
1908	43,605	22,348	21,257
1909	43,163	22,051	21,112
1910	44,595	24,748	19,847
1911	46,547	31,438	15,109
1912	47,262	32,240	15,022
1913	45,348	26,815	18,533

The flasks contain 75 lbs. each. The consumption fluctuates within very wide limits, as shown by these figures. At the commencement of next year the effect of the war will be ascertainable on both the supply and British consumption. In Austria the quicksilver deposits occur in Idria, Western Carniola, and in Italy at Monte Amiata, Tuscany. The Mexican and Russian outputs are very limited in scale; four years ago the Russian output was only 4 tons. The price of quicksilver has risen enormously since the war commenced; the Austrian supply, controlled by the Government, is definitely cut off from the world's markets, and the Italian supply is uncertain. The Spanish supply is controlled mainly in London, and very little may be available for export. American supplies can scarcely be obtainable for export to Europe, as its consumption appears to have overtaken its production. In fact, England has been exporting quicksilver to the United States in small quantities for some years—during 1913, 154,500 lbs., to the value of $74,800.

Quicksilver imported by England was worth $36.27 per flask last year compared with $41.86 during 1911. The war has had a marked effect on English quicksilver imports, as shown by the following figures:

Imports for:		1912	1913	1914
August	lb.	101,779	67,196	1792
	flask	1357	896	24
September	lb.	32,818	61,851	18,240
	flask	437	824	243

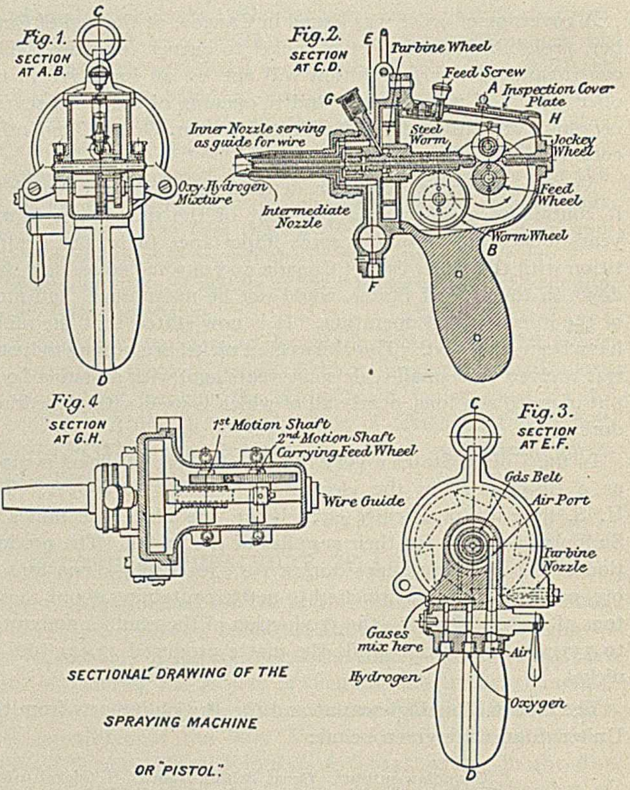
METAL SPRAYING

An interesting device which is just emerging from the experimental stage, is one described in *Engineering* (London), 98 (1914), 382, by R. K. Morcom, for covering objects with a metallic coat by spraying them with molten metal.

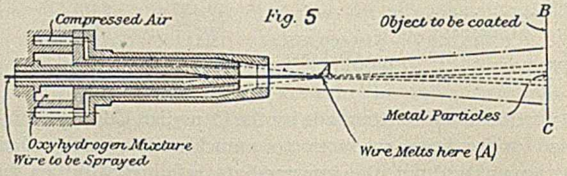
The essential parts of the machine, or "pistol," as it is called, are a combined melting and spraying jet and a feed mechanism. The metal rod or wire is fed to the melting-flame formed by coal-gas, water-gas, acetylene, hydrogen, etc., burning in air or oxygen according to the metal used. The gases are supplied at such pressures as to prevent blowing out and to ensure a highly deoxidizing flame. The spraying jet can be of carbon dioxide, nitrogen, air, steam, etc., and is fed at such a pressure as to produce a sufficiently high velocity for successful coating. The various pressures must be carefully kept constant by accurate gauges and reducing-valves.

The feeding of the wire is accomplished by a small pneumatic motor, driven by the spraying medium either in series or parallel with the main jet. For small work, hand operation is sufficient, but probably, when large work is undertaken, it will prove convenient to have mechanical traverse and control.

The surface to be coated must be thoroughly clean and of an open nature to give a key for the deposit. Sand-blasting with sharp sand has been found best. Such surfaces as fabrics, wood, unglazed earthenware, and asbestos require only freedom from grease. The process in detail is the following:



SECTIONAL DRAWING OF THE SPRAYING MACHINE OR "PISTOL."



DIAGRAMMATIC REPRESENTATION OF MELTING & SPRAYING JETS IN ACTION.

The melting-jet is focused at A, Fig. 5, on the tip of the wire. The spraying-jet, cold from expansion, strongly draws forward the products of combustion in the center of its cone, and by its draught drags off minute particles of metal, either in the plastic or molten state. The central cone, therefore, consists of metal particles, some cooled to solidity, some molten, and some, perhaps, gaseous, surrounded by a protective reducing atmosphere. This cone is hurled forward with great velocity on to the object to be coated, B C, by the outer jet. There is a definite, most economical quantity of gas which should be used in the pistol, this quantity being about 1.5 cu. ft. of hydrogen per minute, and 0.5 cu. ft. of oxygen, or about 0.8 cu. ft. of coal-gas to 0.65 cu. ft. of oxygen for the present standard designs.

As at present constructed, the standard pistol uses for spraying about 0.55 to 0.6 cu. ft. of air per minute for every 1 lb. per sq. in. air pressure, so that with an air supply at 80 lb. per sq. in., which is a very suitable figure for ordinary spraying, the air consumption will be from 45 to 50 cu. ft. per minute. The mass of this will be from 830 to 920 g. and the mass of metal sprayed by this air will be from about 8 g. in the case of iron to about 200 g. in the case of lead. The effectiveness of the cooling is shown by the fact that the hand can be held to receive a coating of metal without inconvenience.

RECENT DEVELOPMENTS IN GERMAN-AMERICAN TRADE IN CHEMICALS

Of all the effects of the war, that on the trade of the various countries involved, as well as of neutral lands, is perhaps, at present, the easiest to evaluate. An attempt to study German export trade as affected by the war is made by Prof. H. Grossmann in an article in *Chem. Ztg.*, 38 (1914), 1169, in which the growth of chemical industries in Germany since the present tariff laws went into effect is studied, and their present situation is compared with that of similar industries of foreign nations. The part of the article of special interest to us is, of course, that dealing with the United States.

The year 1913 probably marks a maximum in international trade, not only for Germany, but for the whole world. In spite of the fears expressed by free traders at the time of the enactment of the German tariff of 1902, and in spite of the increase in foreign customs duties, the German export trade in chemicals has shown a remarkable growth, a fact proved not only by the export statistics and by increased earnings of exporters, but by the increase in wages and number of laborers employed.

Germany is now in the fortunate position, according to O. N. Witt [*Chem. Ztg.*, 38 (1914), 1117, 1130], of having within her own borders enormous quantities of a large number of necessary natural products such as salt, potassium chloride, coal, potatoes, sugar-beets, etc. However, many other raw products must be bought in large amounts from foreign lands, *i. e.*, now, from neutral countries; among these products are many ores and metals, oil seed, fats and oils, saltpeter, iodine, boron compounds, camphor, rubber, tanning materials, animal and vegetable fibers, raw phosphates, calcium acetate, etc. The relative scarcity of some of these has led to a rise in price since the beginning of the war. The following table is given by Grossmann to show the origin and amounts of these substances in 1913:

RAW PRODUCT	METRIC TONS	CHIEF EXPORTERS
ORES:		
Iron pyrites	1,027,000	Spain, Portugal, Norway
Chromium ores	232,000	France, Australia
Tungsten ores	47,800	British India, Australia
Bauxite	384,500	France
Raw phosphates	926,000	U. S. A., Algeria, Tunis
Saltpeter	774,000	Chile
FATS AND OILS:		
Oil fruits	1,747,000	Tropical countries
Vegetable oils, etc.	579,700	Tropical countries
Oil cake	828,000	Tropical countries
Mineral oil, refined	745,000	U. S. A., Austria-Hungary
FIBER STUFFS:		
Cotton, raw	478,000	U. S. A., Egypt, British India
Wool, raw	199,300	Argentina, Austria, British South Africa
Flax	71,200	Russia, Austria-Hungary
Hemp	45,700	Russia, Italy
Jute	162,100	British India
Rubber	20,500	Brazil, Africa, S. E. Asia
Camphor	8,700	Japan
Calcium acetate	20,900	U. S. A.
Iodine	258,000	Chile

The most important German exports in 1913 were:

EXPORT	METRIC TONS	CHIEF IMPORTERS
Sugar, raw	527,000	England
Sugar, crystal	390,000	England
Aniline and coal tar dyes	64,300	U. S. A., England, China, Austria-Hungary
Potassium and "abraum" salts	1,676,000	U. S. A., Sweden, Holland
Potassium chloride	393,000	
Indigo	33,300	China, U. S. A.

Although the chemical industries in the United States have made great progress in the last ten years, they are still dependent on Germany for many products and the same situation exists in England. It has been stated that, with the assurance of high prices and long continued protection, American industries would be able to meet demands in any line of manufacture, but Grossmann points out the difficulty of meeting the first condition, and the fact that already the American duties are not low. Glass, leather and textile manufacturers are already considering whether in case of continued exclusion of German chemical products, it would not be cheaper to close their factories altogether. Although, naturally, there is much discussion in the American press of possibilities of becoming chemically independent of Germany, little has been done practically. Other industries that suffer in this country are agriculture and the electrolytic potash industry from lack of potassium salts, while Grossmann shows among the industries favored by the war is the calcium cyanamide industry.

BENZOL AS A FUEL

The increasing use of benzol as a fuel for motor cars abroad and its probable effect on the price of gasoline were mentioned in THIS JOURNAL, 6 (1914), 259. Germany's present complete isolation from an adequate petroleum supply makes the fuel question one of anxiety and vital importance to her. *The Manchester Guardian* (England) prints statistics showing the growth of benzol production in Germany and its availability at present:

"For further supplies of motor fuel, Germany will turn to benzol. It is as good as petrol, and she makes it herself, both for various industrial purposes and for motor fuel. This has been a growing industry in Germany; and she may surprise us by a further sudden expansion of it. Benzol is obtained as a by-product from coke-ovens. In England only about one-third of such ovens are really adapted for benzol recovery; in Germany every oven is. In 1907 she produced less than 2,000,000 gals. of benzol, and bought about 1,500,000 gals. from us. By 1911 her production had risen to over 6,000,000 gals., and she took only 140,000 gals. from us. Even if the 1911 figures had not been improved upon, Germany cannot starve for motor fuel while her coke-ovens are working. To keep them working, however, entails a supply of coal, and we do not know what her stocks or present output are. It needs 17 tons of coal to produce a gallon of benzol, or 8,000,000 tons a month to maintain the normal benzol supply (on the 1911 figures). In 1912 the German Government ordered a plant capable of producing 6,000,000 gals. of benzol per annum, and three months ago they prohibited the export of benzol to France. It is unlikely that Germany neglected to stock benzol (or the coal to make it) as one of the sinews of war."

In England too, on account of the high cost of gasoline, the use of benzol as a motor fuel has been increasing steadily, but some dissatisfaction has attended its use.

Complaints are frequently received from users that, after a moderate amount of benzol has been used, a sticky deposit is noticed in the crank case, valve-stems, etc., and this eventually interferes with the satisfactory lubrication of the engine [*J. Gas Lighting*, 128 (1914), 184]. There is no doubt that benzol when properly made leaves no such deposit; but it is only too true that much of the benzol put on the market as motor spirit —supposed to be washed and refined—is really unsuitable for the purpose, and its presence is only hindering the development of this outlet for the product. Until quite recently, very little of the benzol manufactured in England was refined in the plants where it was recovered. It was generally exported in bulk in the crude state. In Germany, however, a great deal of attention has for a long time been devoted to the preparation of purified products, and a high state of efficiency has been reached in the washing and refining processes. This latter fact is undoubtedly attributable to the enormous demand for rectified products consequent on the expansion of the synthetic or coal-tar color industry. With the increasing demand for rectified benzol for motor and other industrial purposes in England, refining plants were erected; but even now they are not always operated with the scientific exactitude characteristic of the majority of German industrial organizations. Numerous samples of so-called motor benzol when distilled at 100° to 110° C. leave a fair proportion—sometimes as much as 5 per cent—of dark colored constituents. These should have been eliminated in the washing operations, as undoubtedly their presence has a deleterious effect when the benzol is ultimately used in motor engines.

GERMANY'S ARTIFICIAL FERTILIZERS

Under this title appears in the *Z. Ver. deut. Ing.*, 58 (1914) 1443, an article on the present importance of the fertilizer question in Germany. Three substances are considered: potash, nitrogen and phosphoric acid. As far as potash is concerned, there is no doubt of Germany's superiority over the rest of the world, but conditions are not so favorable as regards nitrogen compounds from natural sources. To overcome this deficiency has been one of the aims of German industry, and as a result the production of ammonium sulfate from the distillation of coal in gas works and coke ovens reached the total in 1912 of 492,000 tons, which far exceeds England's 379,000 or America's 151,000 tons. As a result, the nitrogen used in Germany has more and more been supplied by ammonium sulfate and correspondingly less by saltpeter; 1909 was the first year in which the consumption of the former exceeded that of the latter, and in 1912 the ratio was about 8.7 : 7.8 in favor of ammonia. This comparison shows, however, that large amounts of Chili saltpeter are still being used, and that any sudden drop in the supply of this salt, like that caused at present by the requisitioning by the government of the supplies on hand, must cause disturbance. This condition can be relieved by drawing on the surplus stored by the Ammoniaks-Verkaufsverbände. The coke ovens are still working to full capacity, so that ammonia is being produced in large amounts, but since their continued activity depends on a continued demand, while their best customers, the iron works, have greatly limited their output, other markets for coke must be found. The representatives of the fertilizer industry, therefore, in a meeting on September 18th emphasized the necessity of substituting coke for coal in every branch of industry where it could possibly be done.

To the processes of ammonia recovery from coal distillates must be added the various new processes for the fixation of atmospheric nitrogen. Those developed by Frank-Caro, Birkeland-Eyde, Schönherr and Pauling have the advantage that the production of fertilizer is their chief aim, and that their output, when the prerequisite conditions are fulfilled, can be increased according to demand without regard to other circumstances. However, their output has not yet grown to sufficient size to influence the market to any extent.

In case the war is of long duration, the Germans claim one advantage in the fact that a new process has been recently developed which will permit the nitrogen production together with the coke production to be established on a yet broader foundation. This process, that of Professor Haber, is one for the synthetic production of ammonia from nitrogen and hydrogen, and is especially characterized by cheapness and practicability. Both facts have led to the fear, expressed in various circles, that the introduction of this process will bring about a serious drop in the price of ammonia, and already proposals have appeared in technical gas journals[1] looking to the working up of the gas washings for other products than ammonium sulfate. However much an injury to the coal distilling industry is to be regretted, from the point of view of the general welfare of the German Empire, it is very satisfying to know that the possibility of developing this process insures against an ammonia famine.

As for the third substance, phosphorus in the form of bone meal, calcium phosphate, etc. (guano is used in ever lessening amounts), it is well-known that the phosphorus-containing substances hitherto imported into Germany have been successfully replaced by the Thomas phosphate meal, a by-product of the Thomas steel works. The German Thomas steel industry is the greatest in the world, so that Germany should be independent of the rest of the world for her phosphorus supply as long as these works are in operation.

THE THERMAL PROPERTIES OF STEAM

Until ten or fifteen years ago steam-tables, based on Regnault's experiments, which were for the most part made before 1847, sufficed for all the needs of the practical engineer. The introduction of the throttling calorimeter for the estimation of the quality of steam had, however, led to doubts whether the accuracy of Regnault's results was as great as had been assumed, and these doubts were confirmed when the increasing use of superheated steam showed in many cases gains substantially in excess of the theoretical. Further researches, both theoretical and experimental, on the properties of steam were accordingly undertaken in many countries, and led to the publication of new steam-tables, such as those of Marks and Davis, or the new edition of Professor Peabody's tables, which fully satisfy the present requirements of engineering practice. Further experimental data have, however, been secured since the publication of these tables, and a very complete discussion of the thermal properties of steam, in which cognizance is taken of these newer results, has just been published by Professor G. A. Goodenough.[1]

In this pamphlet [*Engineering* (London), 98 (1914), 624] the whole of the available data is brought into consideration and new formulae established, which, while fitting the experimental results with great accuracy, are also consistent with each other and with thermodynamic principles, a matter of which Professor H. L. Callendar seems to have been the first to recognize the importance.

The relation found between the pressure and temperature of the steam is as follows:

$$\begin{aligned}\log p = 10.5688080 - \frac{4876.643}{T} - 0.0155 \log T \\ - 0.00406258\, T + 0.00000400555\, T^2 \\ - 0.00002 \left[10 - 10 \left(\frac{t - 370}{100} \right)^2 + \left(\frac{t - 370}{100} \right) \right],\end{aligned}$$

where p is the pressure in pounds per square inch, and T the absolute temperature in Fahrenheit units, while t is the temperature in Fahrenheit degrees. The absolute zero is taken as $-459.6°$ F. For the specific volume of the steam Professor Goodenough gives the expression:

$$v - 0.017 = 0.59465 \frac{T}{p} - (1 + 0.05129 \sqrt{p}) \frac{C_1}{T^4}$$

where v denotes the volume in cu. ft. per lb., and $\log C_1 = 10.82500$. The "heat content" of steam at different temperatures and pressures is:

$$\begin{aligned}i = 0.320\, T + 0.000063\, T^2 - \frac{23583}{T} \\ - \frac{C_3\, p\, (1 + 0.342 \sqrt{p})}{T^4} + 0.00333\, p + 948.7,\end{aligned}$$

where

$$\log C_3 = 10.79155.$$

The entropy of superheated steam is given by the relation:

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[1] *Jour. Gasb.-Wasserv.*, Aug. 29, 1914, p. 840.

[1] "Thermal Properties of Steam," by G. A. Goodenough. *University of Illinois Bulletin.* London: Chapman and Hall, Limited. (Price, 35 cents.)

$$s = 0.73683 \log T + 0.000126\, T - \frac{11791.5}{T^2} - 0.25355 \log p - \frac{C_4 p\,(1 + 0.0342\, p)}{T^5} - 0.08085,$$

where

$$\log C_4 = 10.69464.$$

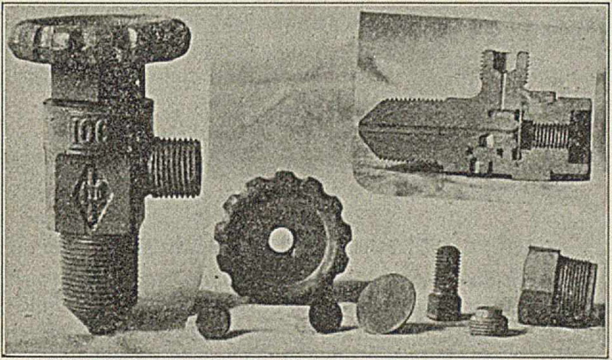
The thermal properties of steam at very high pressures and temperatures are stated to be as follows:

Temperature °F.	Pressure Lbs. per sq. in.	Volume of 1 lb. Cu. ft.	Weight of 1 cu. ft. Lbs.	Heat content of Liquid B. T. U.	Heat content of Vapor B. T. U.	Latent heat B. T. U.
600.0	1540.4	0.272	3.68	604.5	1164	560
620.0	1658.7	0.241	4.15	633.0	1151	518
640.0	2056.6	0.187	5.35	663.0	1136	473
660.0	2360.8	0.151	6.63	700.0	1112	412
680.0	2699.1	0.118	9.86	745.0	1080	335
700.0	3074.5	0.080	12.46	823.0	1016	193
706.3	3200.0	0.048	20.92	921.0	921	0

A HIGH PRESSURE VALVE

The International Oxygen Company laboratory has developed a new valve for pressures up to 2,500 lbs. It is specially recommended for oxygen, hydrogen, nitrogen and similar gases. It is made of metal throughout, no packing being used in any part. The body is forged Tobin bronze, while the other parts are made of suitable metals which are non-corrosive to gases or to any weather conditions. The cross section shows the simple construction of the valve. Every part is accessible and, if worn out, can be easily replaced at little expense.

The diaphragm is made of very tough and springy material that will withstand perfectly all the strain put upon it, without any possibility of its cracking or breaking even after many years of service. The diaphragm takes the place of packing material, and in this way the usual stuffing box is entirely eliminated. In the case of high pressure oxygen gas, the stuffing box is extremely objectionable, as one must resort to the use of rubber, leather or similar inflammable materials.



The diaphragm is slightly concave, and is normally set away from the seat of the valve a sufficient distance to permit a full opening of the valve. It is not necessary, therefore, for the gas to raise the diaphragm; in this way all the gas from the cylinder can be used, down to atmospheric pressure.

An essential part of any high pressure valve is its safety plug. In this valve is a very ingenious device which has received the approval of the Bureau of Explosives of the Interstate Commerce Commission. The plug is filled with fusible metal melting at, or below, the boiling point of water. It is provided with three passages, each in a straight line with the direct action of the gas in the cylinder to permit the outflow of the metal; and is further provided with a hemispherical seat and a phosphor bronze disc. This safety plug is screwed into the body of the valve and forms a tight seat by compressing the phosphor bronze disc. No part of this plug projects beyond the body of the valve, thus protecting it against breakage. The safety will not blow when submitted to the direct rays of the sun or any other atmospheric condition, but will blow when placed in a fire, before the expansion of the gas can do any damage to the cylinder.

OFFICIAL FIRE-TEST WITH TREATED WOOD

The British Fire-Prevention Committee have just issued their report No. 193, regarding a test carried out on July 1 with a match-boarded pine partition, in which the pine was impregnated by a proprietary process, with the object of making it fire-resistant. The partition comprised studs with $^5/_8$ in. grooved, tongued and beaded match-boarding on both sides, and it measured 10 ft. wide by 9 ft. high. The test was conducted under the committee's usual conditions, and was a forty-five minutes' test at temperatures that rose to 1630° F., whereupon water was applied from a stream fire engine. The main features in the official "Summary" of the test are that smoke appeared freely through several joints after thirty-eight minutes, and that after forty minutes, scorching appeared at several joints; further, that after forty-four minutes a glow was seen at four points. Upon the application of water, water came through several of the vertical joints. The fire-resistance was thus considerable for wood-work, although the minimum classification as to such a partition affording "Temporary Protection" under the British Fire-Prevention Committee's Standards—necessitating resistance for forty-five minutes—was not obtained by a few minutes. It would have been interesting if the partition had been tested side by side with a match-boarded pine partition which had not been impregnated.

COAL IN ICELAND

The fear of a coal famine in Denmark on account of the war has caused the coal deposits at Dufansdale, in the Arnar firth, to be examined, according to *Engineering* (London) 98 (1914), 604, and the results of the investigation are understood to be encouraging. The deposits are likely to prove very extensive, and the quality is satisfactory and improves the deeper one gets. They are right upon a firth with excellent anchorage for vessels.

NOTES AND CORRESPONDENCE

ARGON ON A COMMERCIAL SCALE

Editor of the Journal of Industrial and Engineering Chemistry:

We thought it might be of interest to the American chemists to know that during the past week the American Cyanamid Company have been shipping several flasks of one hundred (100) cubic feet capacity, of ARGON, probably the first made on a commercial scale in this country. The manufacture of Argon by this company has been placed upon an industrial basis so that these shipments are being made regularly every day, and in no sense is it an experimental undertaking.

The credit for the development of this industry belongs to Mr. G. A. Hendrie of our company, and we believe it worthy of record that this fact be coupled with his name in the history of American Industrial Chemistry.

American Cyanamid Company
Per W. S. Landis

Niagara Falls, Ontario
December 10, 1914

THE BARBER ASPHALT PAVING COMPANY PRIZES

Editor of the Journal of Industrial and Engineering Chemistry:

The Barber Asphalt Paving Company has decided to offer students in Engineering Schools an opportunity to compete for $1,000 in prizes for essays on highway construction. This offer has been made to twenty engineering schools, including all those of first importance in the country.

Prizes of $50 will be awarded to members of the 1915 classes of each of the leading educational institutions maintaining engineering courses. All papers must be in our hands by June 1, 1915, and no paper can be considered that exceeds 3,000 words in length. If as many as five papers should not be received from the students of any one school the right is reserved not to award a prize to the student of such school. The amount of original thought and investigation shown will be given especial consideration in arriving at conclusions as to the relative merit of papers.

Other subjects than the following or variations of these subjects will be freely permitted, provided that such variations do not go outside of the general subject of Asphaltic Highway Construction.

1—Comparative values of various approved forms of street pavements and roads as regards first cost, cost per year of life, ease of traction, ease of cleaning, noiselessness, dustlessness, etc., etc.

2—A general plan for street and road improvement for a city of 25,000 population, considering traffic in different sections of the city, first cost, cost of maintenance, attractiveness, availability and other factors bearing upon the proper selection of type of construction and materials.

3—Should specifications be drawn so as to admit under the same classification materials of different character, as, for instance, natural asphalts and those made from petroleums?

4—Which is preferable from the viewpoint of the public interest, separate specifications for different classes of material under which the municipality will know exactly what it is getting and pay accordingly; or a single general specification which attempts to cover all grades of materials, and results in making it possible for the contractor who gets the work at the lowest price to use the cheapest materials?

5—Relative value, advantages and disadvantages of laboratory and service tests as applied to the selection of asphaltic materials for highway construction.

6—Field study of an asphalt construction and repair plant, giving organization, output, and cost.

Several of these topics lend themselves especially well to original investigation. A study may be made, for example, of the detailed first cost and cost of maintenance of an actual group of pavements, or the actual paving or highway experience of some community may be studied.

Barber Asphalt Paving Company
Land Title Building, Philadelphia — *Per* D. G. Pierce
December 3, 1914

THE PRESENT POTASH SITUATION

Editor of the Journal of Industrial and Engineering Chemistry:

Judging by the numerous inquiries received, we believe that a statement of the potash situation may be of interest to your readers.

At the outbreak of the war the shipping season for potash from Germany was at its height, but since then the shipments have been made only in limited quantities. The prospect, however, is that they will increase as time goes on. Potash is not contraband of war and none of the nations at war objects to its movement in neutral ships. There is, however, great difficulty in securing railway and river facilities to move it from the mines and storehouses to the coast.

The mines are in good condition and enough workmen not subject to military service are available to keep them in operation.

Most of the leading fertilizer manufacturers have agreed to utilize their present supplies of potash in the effort to produce fertilizers with at least 2 or 3 per cent of potash next spring and the supplies on hand at the outbreak of the war were said to be sufficient for this purpose. There is therefore no reason why farmers should not secure some potash in their goods, although the usual 5 to 10 per cent may not be obtained.

42 Broadway, New York City — H. A. Huston
December 1, 1914

ANOTHER PLATINUM THEFT

Editor of the Journal of Industrial and Engineering Chemistry:

On the night of December 15th our laboratory was entered and platinum to the value of $100 taken.

Suspicion points to a young man who had made two calls at our laboratory asking for information on water, with particular reference to condenser trouble on marine work. The young man had a good knowledge of marine as well as electrical engineering and was familiar with the work on naval training.

He was a neat appearing young man with one exception, that being the stain of tobacco at the corners of his mouth. He was about 35 years of age, stood about 5 ft. 5 in. or 5 ft. 6 in. high, had sandy hair and a reddish face, was freckled, weighed in the neighborhood of 150 lbs. and was undoubtedly of Jewish descent, although he spoke with almost an English accent. He was dressed at the time in a blue chinchilla overcoat, brown soft hat, tan shoes, and dark suit. He also wore a Masonic pin and Chapter charm.

While here he made inquiries regarding other laboratories in this vicinity and we think it possible he intends working around this part of the country.

Thinking you could reach a larger field through This Journal than we could in any way, we are writing you that you may communicate this to the chemists at large and thus avoid further losses at the hands of this person.

Bridgeport Hydraulic Company
Bridgeport, Connecticut — F. C. Barrows, *Chemist*
December 18, 1914

ANNUAL MEETING OF THE CHEMISTS' CLUB

The annual meeting of The Chemists' Club, New York, was held in Rumford Hall on December 9th. The meeting was called to order by President McKenna and the reports of the various committees for the past year were submitted for consideration and action by the membership of the club. The committee appointed to canvass the ballots for the election of officers for the coming year reported the results of the vote, which were announced by the Chair as follows: *President,* M. C. Whitaker; *Resident Vice-President,* B. C. Hesse; *Non-resident Vice-President,* E. R. Grasselli, of Cleveland; *Treasurer,* Albert Plaut; *Secretary,* Reston Stevenson; *Trustees,* T. R. Duggan and P. C. McIlhiney.

As a result of the careful analysis of the operation of the Club for the three years during which it has been in the new clubhouse, the membership unanimously authorized an increase in dues, in order to strengthen the financial position of the organization and at the same time to wipe out the deficits which have accumulated as a result of its greatly enlarged policy. The new scale of dues thus established is $50 per year for resident members, $12.50 for non-resident members, and $15 for junior members.

The balance sheet of the treasurer's report shows a most healthy financial condition of the Club, with a large asset balance. Notably substantial increases in the equipment of the Library were reported, and the close of the present fiscal year leaves the Club in a highly satisfactory condition.

PERSONAL NOTES

A meeting of the Perkin Medal Committee was called at the Chemists' Club on December 7th by President G. W. Thompson. The proposals for candidates for the Perkin Medal for 1914 were carefully discussed. Edward Weston was the unanimous choice of the committee for the medal to be conferred by the New York Section of the Society of Chemical Industry at its regular January meeting.

Arthur D. Little, Inc., of Boston, have established a popular journal of industrial chemistry, known as "The Little Journal." This journal will be published monthly and contain information in regard to industrial processes, products and plants, written in a popular but authoritative style. The first issue, which was put out in December, consisted of 20,000 copies and will be mailed without charge upon request.

The University of Michigan Section of the A. C. S., at its regular meeting on November 24th, elected the following officers: *Chairman,* L. H. Cone; *Councilor,* S. L. Bigelow; *Secretary-Treasurer,* H. H. Willard; *Executive Committee*—M. Gomberg, W. G. Smeaton and B. W. Peet.

Mr. F. P. Dewey, of the Bureau of the Mint, presented a paper on "The Recovery of Osmiridium in the Electrolytic Refining of Gold," before the Chemical Society of Washington, on December 10th.

Dr. C.-E. A. Winslow has resigned from the College of the City of New York to become director of education in the reorganized State Department of Health. His work at the American Museum of Natural History will continue as heretofore.

Mr. Henry A. Gardner, assistant director of the Institute of Industrial Research, Washington, D. C., spoke on the "Technology of Various Painting Materials" before the Rochester and Syracuse Sections of the A. C. S., on the 7th and 8th of December, respectively.

The 28th meeting of the Connecticut Valley Section of the A. C. S. was held at Springfield on December 12th. In the afternoon the Section toured the plant of the Hendee Manufacturing Company at Winchester Square, State Street. In the evening Mr. Carleton Ellis delivered an address on "Progress in the Hydrogenation of Oils."

Prof. L. H. Harris, formerly associate professor of the University of Pittsburgh, has been appointed consulting engineer to the Public Service Commission of Pennsylvania.

The December meeting of the Iowa Section of the A. C. S. was held December 12th, at Coe College, Cedar Rapids. Dr. Herman Schlundt, of the University of Missouri, spoke on the subject, "Radio-Activity of Waters;" Mr. L. H. Goebel, of the Cedar Rapids Water Works, presented a paper on the "Purification of Water." Afternoon excursions were made to the Starch Works, Quaker Oats Plant, and Packing House.

Mr. A. Fleck, demonstrator at the University of Glasgow, has been appointed physical chemist to the Glasgow Radium Committee, established to administer a large fund collected in the city for the purpose of acquiring and distributing radium for therapeutic purposes. Under the auspices of the committee, a radiometric laboratory has been fitted up at the university.

The 3rd regular meeting of the Maryland Section of the A. C. S. was held on December 19th. Dr. Ira Remsen read a paper on "Reminiscences of Liebig and Wohler."

Prof. H. A. Huston, of the German Kali Works, gave a lecture on "The Potash Industry," illustrated by lantern slides and motion pictures, before the Gamma Chapter of Phi Lambda Upsilon and the Institute of Arts and Sciences of Columbia University, on December 10th.

Mr. James G. Callan, of Arthur D. Little, Inc., Boston, addressed the Rhode Island Section of the A. C. S. on "Abrasives," on December 17th.

At the December meeting of the Detroit Section of the A. C. S. on the 18th, the following program was presented: "The Bleaching of Shellac," by Mr. C. T. Bragg, of Berry Bros.; "The Manufacture of Chemical Porcelain in Detroit," by Mr. Harry Spurrier, of the Jeffery-DeWitt Co.; "The Manufacture of Insulated Wire," by Mr. Jas. H. Bogart, of the Detroit Insulated Wire Co.; "Comparison of the Pharmacopoeias of Different Countries," by H. T. Graber, of the Digestive Ferments Co.; "Some Features of the Gas Industry," by Leigh E. Worthing, of the Detroit City Gas Co.

Dr. Arthur Romaine Hitch, formerly assistant instructor in chemistry at Cornell University, and research chemist of the Solvay Process Co., Syracuse, N. Y., has been appointed instructor in chemistry at the Rice Institute, Houston, Texas.

Prof. William J. Gies, of Columbia University, delivered an address on "The Chemical Investigation of the Cause and Prevention of Dental Caries," before the Philadelphia Section of the A. C. S. on December 17th.

The Pittsburgh Section of the A. C. S., at its meeting on December 17th, gave the following program: "The Freezing of Nitroglycerin and Its Detonation by Shock," Dr. Harold Hibbert, Mellon Institute, University of Pittsburgh; "Protein Charts," Prof. Alexander Silverman, University of Pittsburgh; "A New Process for the Manufacture of Steel," Isador Ladoff, Westinghouse Electric and Manufacturing Co.

Mr. Francis A. J. Fitzgerald lectured on "Thermitite" before the Western New York Section of the A. C. S. on December 17th.

Dr. M. L. Crossley, professor of organic chemistry at William Jewell College until 1913, and lecturer in Wesleyan University, 1913–1914, has been appointed associate professor and acting head of the Department of Chemistry in Wesleyan University. Dr. H. Lee Ward has been appointed associate professor in the department.

The *Chemical Abstracts* index began going into the mails on December 22nd. This number contains 7653 titles and the mailing of the entire issue involves the handling of six and one half tons of paper.

The Chicago Section of the A. C. S. held its December meeting on the 11th. The occasion was the Section's regular "Ladies' Night" and the program consisted of a series of Industrial Motion Pictures, showing the Iron and Steel Industry, Lead Mining, and Paint Manufacture from start to finish.

The following associates have been added to the editorial staff of the Anesthesia Supplement of the *American Journal of Surgery*: Prof. Charles Baskerville, head of the department of chemistry in the College of the City of New York; Prof. Dr. Guido Fisher, director of the Royal Dental Institute of the University of Marburg, Germany; and Dr. Torrance-Thompson, of Edinburgh.

The Revision Committee of the United States Pharmacopoeia announce that they have adopted the suggestions formulated by Dr. Charles Baskerville, in regard to the standards for purity of ether.

Prof. W. D. Bancroft was the guest of honor at an informal dinner given by the Pittsburgh Sections of the American Electrochemical Society and the A. C. S., previous to their joint meeting on December 10th.

GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

DEPARTMENT OF AGRICULTURE

Food and Drugs Act, Etc. The solicitor of this department has issued a compilation under the following title: Food and Drugs Act, June 30, 1906, and amendments of August 23, 1912 and March 3, 1913, with the rules and regulations for the enforcement of the act, food inspection decisions (40–155), selected court decisions, digest of decisions, opinions of the Attorney-General, and appendix. The completeness of the work makes it of value; the material although previously published is scattered through many small publications, some of which are difficult to obtain at this time. The present work, bound in half leather, is for sale by the Supt. of Documents at $1.00.

Decomposition of Soil Carbonates. W. H. MacIntire. Separate from Journal of Agricultural Research, **3**, 79–80. Best obtainable in this journal.

The Microbic Content of Indoor and Outdoor Air. C.-E. A. Winslow and W. W. Browne. Monthly Weather Review, **42**, 452–3. A report of a series of tests on 353 samples of air from various sources showing the range in bacterial content.

A Nitrogenous Soil Constituent, Tetracarbonimid. Edmund C. Shorey and E. H. Walters. Separate from Journal of Agricultural Research, **3**, 175–8. Contribution from the Bureau of Soils.

The Production and Fertilizer Value of Citric-Soluble Phosphoric Acid and Potash. William H. Waggaman. Department Bulletin 143, from the Bureau of Soils. 12 pp. Paper, 5 cents. This paper gives the results of the tests made to determine the fertilizing value of a slag made from a mixture of phosphate rock and feldspar; it is of interest to those engaged in investigations of fertilizer materials.

The Nitrogen of Processed Fertilizers. Elbert C. Lathrop. Department Bulletin 158, from the Bureau of Soils. 24 pp. Paper, 5 cents. This article reports on an investigation of the changes which occur during the manufacture of some of the processed fertilizers, and of the character and availability of the resulting materials when used in farm practice as a part of mixed fertilizers.

PUBLIC HEALTH SERVICE

The Chemical Disinfection of Water. Earle B. Phelps. Public Health Reports, **29**, 2709–15. (Obtainable as part of No. 41, 5 cents.) This is a simple and brief review of the value and importance of this system of water treatment, including a description of simple apparatus by which some of the effective methods may be applied on short notice.

The Source and Supply of Medicines. Martin I. Wilbert. Public Health Reports, **29**, 2715–8. (Obtainable as part of No. 41; 5 cents.) The article has special reference to the interference of drug supplies by the European war conditions. The advantages of encouraging production of these drugs in America and of establishing an American drug distributing center, are pointed out.

SMITHSONIAN INSTITUTION

Smithsonian Physical Tables. (By Thomas Gray.) Frederick E. Fowle. Publication 2269, Smithsonian Miscellaneous Collections. This is the sixth revised edition of the well known set of tables. Price will be given on application.

BUREAU OF MINES

United States Coals Available for Export Trade. Van H. Manning. Bulletin 76. 15 pp. Paper, 5 cents. Data and average analyses are given for the available coals, with special attention to the questions of hardness, resistance to breakage in handling and other physical properties. In each case such data are given as would be useful in judging the suitability of the coal for special uses. This is also available in Spanish and Portuguese.

Analyses of Mine and Car Samples of Coal Collected in the Fiscal Years 1911 to 1913. Arno C. Fieldner, Howard I. Smith, Albert H. Fay and Samuel Sanford. Bulletin 85. 444 pp. Paper, 45 cents. This is a compilation of analyses with descriptions of the coals collected by the Bureau of Mines, the Geological Survey and in a few cases by state officials, the data being arranged by locality of the mine or prospect from which it was taken. It would be mainly useful in the study of the character of fuels available in various localities; but no generalizations or summaries are given.

BUREAU OF STANDARDS

Combustion Calorimetry and the Heats of Combustion of Cane Sugar, Benzoic Acid, and Naphthalene. H. C. Dickinson. Scientific Paper No. 230. 67 pp. This article gives a general review of the methods and factors affecting accuracy of bomb calorimetry and includes a discussion of the principles of calorimetric design and calibration. The values given for the various substances are as follows: Naphthalene 9622 ± 2 (20°) calories per gram weighed in air, benzoic acid 6329 ± 2 (20°) calories per gram weighed in air, sucrose or cane sugar 3949 ± 2 (20°) calories per gram weighed in air.

Standardization of No. 200 Cement Sieves. Rudolph J. Wigg and J. C. Pearson. Technologic Paper No. 42. 51 pp. This paper discusses the results of a number of observations made to determine methods of standardizing the 200-mesh sieve and its manipulation, so that greater uniformity may be obtained in its use. In the course of the investigation a study has been made of the following:

(1) The accuracy of sieving tests, personal equation in sieving, variations in sieving values of standard sieves, and precautions necessary in sieving tests.

(2) The results of sieving tests made in 85 different laboratories and a comparison of these results with those obtained by the Bureau of Standards on some of the same sieves.

(3) Four proposed methods of standardizing sieves.

(4) The suitability of a number of finely ground materials, as compared with Portland cement, for use in calibrating sieves.

(5) The adoption of a standard value of fineness.

(6) The application of a "correction" to the sieving value of standard sieves.

(7) A revised specification for standard sieves.

Copper Wire Tables. Circular No. 31, 3rd edition. 70 pp. This is a reprint, with a few changes, of the circular of the same name issued about a year ago. It is accompanied by a card of copper wire tables giving in English and metric units a working table for standard annealed copper wire according to the American wire gage (B. & S.).

Fees for Electric, Magnetic, and Photometric Testing. Circular No. 6, 6th edition. 27 pp. This is a revised and extended edition of this publication which gives tabulations of the charges and the character of tests made by the Bureau of

Standards on electrical, magnetic and photometric testing instruments.

Testing of Glass Volumetric Apparatus. Circular No. 9, 7th edition. 31 pp. A revised and extended statement of standard specifications for glass volumetric apparatus, such as flasks cylinders, pipettes, burettes, etc., including the rules of the Bureau regarding apparatus which will be accepted for test and the character of and charges for certification of this apparatus.

CONSULAR REPORTS—NOVEMBER, 1914

From the cashew-nut in India, there is obtained an **edible oil** (similar to almond oil), and from the shells a fluid called "cardole" used to **protect wood** from white ants. (P. 566.)

Owing to the scarcity of **dyestuffs** the prices for dyeing in England have been raised from 5 to 20 per cent above normal. (P. 567.)

The price of **"60 per cent acetic acid"** in England for use in the manufacture of vinegar, has risen from $90 to $140 per ton. (P. 569.)

The output of **sumac** from Sicily has shown a decided decrease in recent years. (P. 573.)

A company has been organized to prospect for **magnesite and manganese ore** near Pisa, Italy. (P. 608.)

A **potash** survey in Spain has shown the existence of marketable amounts near Barcelona. (P. 615.)

Recent Demands for American Goods Owing to the War (pp.)

Switzerland—552
Petroleum
Gasoline
Transformer oil
Copper
Tin
Forged steel
Leather

Russia—585
Medicines
Absorbent cotton
Iron

Belgian Kongo—586
Coal
Machine oil
Calcium carbide
Petroleum
Olive oil
Matches
Candles
Anhydrous ammonia
Lead subacetate
Alcohol
Caustic alkali
Miscellaneous drugs and chemicals

Norway—593
Hardware
Electrical supplies
Sugar
Oleo oil

Ireland—600, 602 and 789
Window glass
Lamp chimneys
Nails
Barbed wire

Spain—673
Auto tires
Electrical supplies
Aluminum
Tool steel
Petroleum products
Pitch
Resin
Tallow

New Brunswick—678
China
Glass
Porcelain
Celluloid

India—682 and 865
Chemicals
Dyes
Glassware
Matches
Paper
Salt

Argentine—689
Naphtha
Iron
Petroleum
Lubricating oils

Greece—692
Sugar
Copper sulfate
Coal
Copper
Iron

China—695
Aniline dyes
Window glass
Indigo
Iron
Paper

British Honduras—713
Coal

France—716
Linseed
Wood pulp
Sodium nitrate
Sulfur
Petroleum
Coal
Coal tar
Super-phosphate
Chemical
Pottery
China
Glassware
Rubber goods

Algeria—721
Sugar
Petroleum
Gasoline

Canary Islands—726
Sugar
Condensed milk
Lard

Costa Rica—732
Beer
Paints
Perfumes, etc.

Norway—742
Cottonseed meal
Tallow
Electrical machinery
Kerosene

Brazil—752
Potato starch

Mexico—761
Wood pulp
Writing paper

Denmark—767
Paper
Paper stock
Petroleum
Gasoline
Oils
Varnishes

Guatemala—781
Enameled ware

Harbin, China—782
Electrical supplies
Dental supplies
Paper
Drugs
Photographic supplies
Tin
Galvanized iron

Ceylon—792
Beer
Cement
Corrugated iron
Hardware
Paper
Glass

Norway—812
Coals

Amoy, China—814
Fertilizer
Matches
Paper

Formosa—871
Petroleum
Iron and steel
Condensed milk

Swatow, China—899
Dyes
Enameled ware
Candles
Matches
Condensed milk
Paper

Canton, China—914
Varnish
Paints
Oils
Perfumes
Explosives
Drugs
Condensed milk
Electrical apparatus

British Columbia—919
Cream of tartar
Olive oil
Soap
Hardware
Drugs
Paints
Asbestos board
Electrical supplies
Glass

Andalusia—929
Iron
Hardware
Enamel ware
Electrical supplies
China
Glass
Dyes
Drugs
Paints
Cement
Paper
Phosphate

Statistics, etc., on Exports during 1912 and 1913 to the U. S. (pp.)

China—649 and 849
Albumen
Antimony
Bean (soya) cake
Bristles
Camphor
Cassia
Galls
Hides
Pig iron
Jute
Linseed
Musk
Peanuts
Bean oil
Cottonseed oil
Peanut oil
Rapeseed oil
Wood oil
Rhubarb
Soap stock
Vegetable tallow
Tin
Turmeric
Beeswax
Yellow wax

Norway—744
Seaweed ash
Chemicals
Fertilizer
Hides
Matches
Cod-liver oil
Paper
Wood pulp

New Zealand—774
Coals
Gold
Kauri gum
Hides
Tallow

The **nitrate** industry of Chili is almost paralyzed in spite of the efforts of the government to keep the plants in operation. (Pp. 685 and 819.)

Shortage of **chemical wood-pulp** in England is caused by the curtailment of production in Norway and Sweden, due to lack of fuel and chemicals. (P. 688.)

Bean meal obtained in Manchuria as a by-product in extracting soya beans with solvents, is preferable as a **fertilizer** to bean cake, obtained by expressing the oil from the beans. (P. 699.)

The Standard Oil Company has just completed a new **oil refinery** at Tampico, Mexico. (P. 777.)

Papyrus and tambookie grass are to be used in South Africa as **raw material for paper.** (P. 891.)

After extensive experiments, the Department of Agriculture of Ireland has concluded that while **sugar beets** can be successfully grown in Ireland, their culture would not be profitable. (P. 926.)

GEOLOGICAL SURVEY

Contributions to Economic Geology 1912. Part 2—Mineral Fuels. M. R. Campbell, Geologist in charge. Bulletin 541. 532 pp. 29 plates. Paper, 50 cents. This bulletin includes 26 brief reports on mineral occurrences of economic interest and preliminary reports on economic investigations. Most of these reports have been mentioned already in This Journal at the times when they were issued as separates.

Contributions to Economic Geology 1913. Parts 1 and 2. Additional reports which will make up Bulletins 580 and 581 have been issued recently as follows:

(1) **The Phosphate Deposits of South Carolina.** G. S. Rogers. Bulletin 580 J. 37 pp.

(2) **Ore Deposits in the Sawtooth Quadrangle, Blaine and Custer Counties, Idaho.** J. B. Umpleby. Bulletin 580 K. 28 pp.

(3) **Salines in the Owens, Searles, and Panamint Basins, Southeastern California.** H. S. Gale. Bulletin 580 L. 72 pp.

(4) **Rutile Deposits of Eastern United States** (with information concerning some foreign deposits of rutile). Thomas L. Watson. Bulletin 580 O. 27 pp.

(5) **The Moorcroft Oil Field and the Big Muddy Dome, Wyoming, Papers.** V. H. Barnett. Bulletin 581 C. 34 pp. These papers describe geological investigations regarding the presence of oil in these districts. The work in the first district is not encouraging to further development of the field; in the second district further tests are needed.

(6) **Geologic and Oil Prospects in Waltham, Priest, Bitterwater and Peachtree Valleys, California, with Notes on Coal.** Robert W. Pack and Walter A. English. Bulletin 581 D. 41 pp.

Slate in the United States. T. N. Dale and Others. Bulletin 586. 220 pp. and 26 plates. Paper, 50 cents. "This volume is not only a corrected and revised edition of Bulletin 275, Slate Deposits and Slate Industry of the United States, but also contains the results of all recent discoveries and studies of slate in this country. Its plan is (1) to set forth, in succinct form, the present state of scientific knowledge as to the origin, structure, texture, and chemical and mineral composition of slate; (2) to describe in more or less detail the slates and quarries of each district; and (3) to consider the economic geology of slate, including scientific prospecting for it, methods of testing it, slate machinery, and the use of slate and slate waste, together with a tabular summary of all the slates described."

The Constitution of Natural Silicates. F. W. Clarke. Bulletin 588. 128 pp. Paper, 15 cents. The announcement of this bulletin indicates its importance as follows: "This bulletin presents the results of a study of the chemical structure of the silicates found in the solid crust of the earth. From the geologist's point of view the silicates are of fundamental importance, for they form at least nine-tenths of the entire known mass of the earth's crust, and a study of their inner constitution may be reasonably expected to shed light upon many serious problems. Every primitive rock or eruptive mass contains an aggregation of silicates, each one capable of undergoing chemical change by which alteration products are formed, so that in time the rock may become transformed into new substances, quite unlike those which originally existed in it. A knowledge of the processes which thus occur, dependent on chemical structure, should be applicable to the study of the rocks and should ultimately render it possible, by investigating a metamorphosed mass, to clearly indicate its origin."

Quality of the Surface Waters of Oregon. Walton Van Winkle. Water-Supply Paper 363. 137 pp. Paper, 20 cents. This bulletin which was prepared in coöperation with officials of the State of Oregon gives "a brief discussion of the constituents, uses, and purification of natural waters and a detailed consideration, by drainage basins, of the quality of the stream waters of Oregon, showing the nature and amount of the materials they hold in solution. The paper contains many analyses, which show that the river waters of Oregon are low in mineral content and are very good for general industrial use and for irrigation."

Water Analyses from the Laboratory of the U. S. Geological Survey. Tabulated by F. W. Clarke. Water-Supply Paper 364. 40 pp. Paper, 5 cents. This bulletin contains 203 analyses, made in the chemical laboratory of the United States Geological Survey, of waters from rivers, lakes, wells, and springs in the United States as well as some mine waters. Most of these analyses have been published elsewhere, but many of the original documents are out of print and are therefore obtainable with difficulty.

Mineral Resources of the United States, Calendar Year 1913. In addition to those sections previously announced, separates of the following subjects have been issued; these will be reviewed next month in detail: Gems and Precious Stones, including a discussion of the metric carat; Clay-working Industries; Metals and Metallic Ores; Iron ores, Iron and Steel; Cobalt, Molybdenum, Nickel, Tin, etc.; Gold and Silver; Lead; Platinum Metals; Zinc and Cadmium; Antimony, Arsenic, etc.; Coke; Natural Gas; Fuel Briquetting; Asphalt, etc.; Borax; and Stone.

BOOK REVIEWS

Anesthesia. By James Taylor Gwathmey, M.D. in collaboration with Charles Baskerville, Ph.D., F.C.S. New York and London: D. Appleton and Company, 1914. xxxii + 945 p., 283 illus. Price, $6.00.

This comprehensive, distinctly modern treatise bears witness not only to the activity and success of the author and collaborator—the one a professional anesthetist of rare skill and resource, the other a scientist whose investigations on the chemistry of anesthetics have been noteworthy—in the improvement of anesthetic methods, but also to their industry and zeal in getting the work of others into a most convenient form. The amount of labor expended in the preparation must have been enormous; the whole field of rational and technical anesthetics is covered in a way planned to be helpful to the researcher and practitioner alike, and the value of the work is further enhanced by the systematic method of arrangement. While it is not exactly a composite book, ten specialists have contributed chapters.

This work differs from the others on anesthesia in properly devoting a large amount of space to the chemistry of both anesthesia and anesthetics; in supplying the most modern practice for the active practitioner and student; in suggesting many lines for further investigations; and in containing much matter hitherto never considered, or only very superficially considered, in similar treatises. It is indeed original in both plan and execution.

Twenty-one chapters consider in order: the history of anesthesia, general physiology of inhalation anesthesia, the use of rebreathing in the administration of anesthetics, nitrous oxid, ether, ethyl chlorid, chloroform, the selection of the anesthetic and technique for special operations, treatment before, during and after anesthesia, anesthesia by intratracheal insufflation, colonic anesthesia, sequestration method of anesthesia, local anesthesia, intravenous anesthesia, local anesthesia as applied in dentistry, spinal analgesia and spinal anesthesia, electric analgesia, sleep and resuscitation, mental influence in anesthesia, hypnosis in anesthesia, therapeutic uses of inhalation anesthetics, the medico-legal status of the anesthetist, a list of anesthetics, and statistics. There are three appendices: ethyl ether (supplementing Chapter V), chloroform (supplementing Chapter VII), and oxygen. The index, which occupies 48 pages, appears to be quite well done.

It is a meritorious work and one which, it may be predicted, will have a long and useful career, but it is not, unfortunately, free from marked errors of judgment and proof-reading; moreover, some important omissions occur.

It is not clear why, if the reputable houses are "anxious to provide drugs of the highest purity" (p. xi), "close chemical supervision does not always obtain" at the plants thereof. Certainly it is simple enough to prepare anesthetics of pharmacopoeial grade, and a reputable manufacturer would hardly tolerate carelessness in such operations.

As to the text of the book, it may first be indicated that, owing to the very large number of references to medical, chemical and legal literature, a journal list should have been included; and that, in order to complete the excellent chemical considerations, the detection of chloroform and ether and the estimation of these in the cadaver should have been discussed.

Other critical comments may be made as follows: Hickman was not the author of the paper referred to on p. 5, and the "general properties" of ethyl chloride were not discovered by Carlson in 1896 (p. 27; cf. p. 251). On pp. 32 to 56, the authors give a presentment of the theories on the mode of action of anesthetics. They appear to have been unencumbered with preconceived notions and to have been uninfluenced by the perhaps too general acceptance of the Meyer-Overton theory; and while they are disappointingly uncritical, except on p. 39, the statements of fact given in their conclusions (p. 55) are impartial and suggestive, if rather noncommittal. In this connection, the reviewer would suggest that the theories be suitably classified in the next edition; that, since "no attempt has been made to catalogue all the theories proposed," Spencer's valueless explanation be omitted; that Loewe's important theory of narcosis be considered; and that the exceptions of Vernon and Winterstein to Traube's theory (p. 42) be included. Apropos of the Meyer-Overton theory, it would be interesting to ascertain whether the sensitivity of the nervous system toward anesthetics could be increased by withdrawal of lipoids. Mention might be made of the considerations of Garrod on p. 61. Page 85 is not correctly titled. It seems to the reviewer that the action of oil of bitter orange peel (p. 96) is to be attributed solely to its greater penetrating power and therefore to its ability to mask the odor of ether, and not to an obtunding action on the olfactory nerve; the action is analogous to that of the power of eriodictyon to disguise the taste of quinine. Certainly there is nothing "mysterious" in the utilization of a more odorous substance to disguise the scent of another. Figure 64, on p. 201, is inverted. Names of the manufacturers appear on the containers shown in Figs. 63 A, 64 and 117 (see also Figs. 52, 77–79, 82, 123 and 131), and not on those illustrated on p. 254. This, notwithstanding the fact that the authors did not consider it "desirable to indicate from whom certain instruments could be obtained" (p. x). The large footnote on p. 282 should have been worked into Chapter I. Footnote 2 on p. 288 is largely repeated in the text on p. 300; reference might have been made here to the "narcosis progression" analyzed by Graham Brown, in connection with which the recent work of van Leeuwen (*Arch. ges. Physiol.*, **159**, 291) is of interest. On p. 371, it should have been noted that 'when atropin is mentioned, reference is not had to the eclectic preparation' (the authors employ simplified chemical orthoepy). The use of phenyldihydroquinazoline tannate in vomiting following narcosis is not referred to on p. 379. The mechanism of oil-ether colonic anesthesia might have been further elucidated by regarding it as a "transgression" process (p. 462); this process is discussed by Morgenroth and Ginsberg in *Zentr. Augenheilk.*, **37**, 315. The physiology of local anesthesia is not discussed in Chapter XIII; much remains to be explained in this field; for instance, the actions of many local anesthetics on nerve endings and nerve trunks are not always parallel. It is not generally recognized that solubility in fat influences the results (on this point, see Fromherz, *Arch. exp. Path. Pharm.*, **76**, 257). The production of local anesthesia by cataphoresis should have received 400 words at least; a good discussion of this procedure is contained in *Hygiea*, **75**, 184. On p. 645, "Lister" should read "Liston" (cf. p. 20), and poor proof-reading occurs in line 9 on p. 677. Chapter XIX, on "The Medico-Legal Status of the Anesthetist," contains an excellent account of the physician's liability, which every practitioner might read with profit. The author of this chapter, Mr. J. W. H. Crin, states that "it is to that higher law, the ethics of the medical profession, that society must ultimately look for protection:" quite true, but far removed from the pettier aims of mere financial betterment, ethics points the way to a goal of illimitable loftiness; no matter what rules of conduct obtain in the medical profession, as in others having similar codes, it must be remembered that the moral conceptions of different individuals are widely variant. A physician may become a specialist upon his own determination (p. 684): it has been reasonably proposed that the peculiar skill requisite to so qualify him should be determined by the state medical boards, upon a procedure laid down by the American Medical Association.

Chapter XX, "A List of Anesthetics," which occupies 152 pp., is rich in bibliographic data and should be of great value for reference purposes; this chapter is, in fact, the most noteworthy section of the book, and it is evident that much time was spent in collecting the facts presented; it alone would repay those interested for the purchase of the book. Some of the bibliographies (as those on pp. 690, 694, 700, 724, 751, 766, 784, 790, 800, 807, 812 and 833) are arranged chronologically or approximately so, while others (as shown on pp. 740 and 820) are classified alphabetically according to authors' names; moreover, these bibliographies are not indexed. "Snape's calorific fluid" and "Nabolis," while mentioned on p. 536, are not included in this list; under "Air" (p. 692), it should have been noted that liquid air has been used in the production of local anesthesia in dental practice; on p. 703, line 33, reference is had to the preparations of Schleich (p. 810) and not to a treatise; it might have been noted on p. 713 that the lipoid-solubility of benzene plays a role in its action (see *Biochem. Z.*, **61**, 372); the alkaloid cevine, which produces local anesthesia, is not mentioned; papaverine, a 10 per cent solution of whose sulfate produces complete anesthesia of the conjunctiva, is omitted; potassium sulfate and chloride produce marked local narcosis (see, among others, Zorn, *Z. exp. Path. Ther.*, **12**, 529), but are not included; only *l*-scopolamine hydrobromide should be used in practice—a fact which is not mentioned on p. 810; thymacetol, the acetol ester of thymotinic acid, and possessing a pronounced local anesthetic action, is not included; and "Zeuner's Halspastillen" should not have appeared as a form of "Yohydrol." A question of interest arises in connection with quinine and urea hydrochloride (p. 805) local anesthesia; is this action due to the compound *per se* or to the formation of carbon dioxide by hydrochloric acid in the tissues? Filippi (*Lo Sper.*, **66**, 383) explains the result by the action towards lipoids peculiar to both urea and carbon dioxide; an explanation is then afforded by the Meyer-Overton theory. Since yohimbine hydrochloride possesses anesthetic properties, it would be interesting to determine the action of its isomer, corynanthine hydrochloride.

W. A. Hamor

Chemical Technology and Analysis of Oils, Fats and Waxes. By J. Lewkowitsch, edited by George H. Warburton. Fifth Edition, Vol. II. Macmillan and Company, London, and the Macmillan Co., 66 Fifth Avenue, New York, 1914. Price, $6.50.

Since the death of Dr. Lewkowitsch the revision of his well known treatise has been carried on by Mr. Warburton who for seventeen years was his associate. The plan, scope, and style of the work remain unchanged. The present volume covers the same ground as Vol. II of the fourth edition, but contains 944 pages as against 816 pages in the latter volume. A short section on denaturing oils and fats has been introduced and a number of oils and fats not previously regarded as sufficiently important to require mention are now described briefly. In the main however, the increase in size is due to new matter incorporated in the descriptions of the sources, preparation, analytical characters, and probable adulterants of the various oils, fats and waxes of commerce.

Statistical data are quoted freely and are brought rather closely down to date, the tables of figures for different years ending usually with 1911, 1912, or (in a few cases) 1913. Extended tabulations of chemical and physical characteristics continue to be a prominent feature of the descriptions of the individual oils and fats. In these descriptions there is relatively little discussion of the detailed technique of preparation and refining. The first thirty eight pages of the volume are devoted to a general chapter on commercial preparation, but the full description of manufacturing operations employed in the individual oil and fat industries is apparently reserved for the concluding volume.

The present volume gives evidence of more thorough revision than is usual in books of its size and appears to cover its allotted field more thoroughly than any other single work. It contains a detailed table of contents in which the materials of each group are arranged (as in earlier editions) in the order of their iodine numbers, and an index of botanical and zoölogical names, but no index of subjects. A general index for the entire work is promised with Vol. III which, according to the preface of the present volume. is already in press.

H. C. Sherman

NEW PUBLICATIONS

By John F. Norton, Massachusetts Institute of Technology, Boston

Assaying in Theory and Practice. By E. A. Wraight. 8vo. 324 pp. Price, $3.00. Longmans, Green & Co., New York.

Chemical Engineering: Notes on Grinding, Sifting, Separating and Transporting Solids. By J. W. Hinchley. 8vo. 112 pp. Price, $0.75. Churchill, London.

Colloids: Ueber die Bedeutung des Lichtes für die Bildung und Stabilität Kolloider Lösungen. By H. Nordenson. 8vo. 164 pp. Price, $1.25. Upsala.

Copper Alloys: British Standard Specification for Copper-Alloy Three Piece Unions. By Engineering Standards Committee. Folio. Price, $1.25. C. Lockwood, London.

Electrochemistry: Laboratory Course in Electrochemistry. By Oliver Patterson Watts. 16mo. 148 pp. Price, $1.00. McGraw-Hill Book Co., New York.

Ferments: Abwehr fermente. Das Auftreten blutfrenider Substrate und Fermente im tierischen Organismus. By E. Abderhalden. 4th Ed. 8vo. 404 pp. Price, $3.00. Berlin.

Food Products. By H. C. Sherman. 8vo. 594 pp. Price, $2.25. The Macmillan Co., New York.

Management: The Science of Works Management. By J. Batey. 12mo. 223 pp. Price, $1.25. D. Van Nostrand Co., New York.

Testing: Resistance of Materials. By Stephen Elmer Slocum. 8vo. 210 pp. Price, $2.00. Ginn & Co., Boston.

Minerals: The Deposits of the Useful Minerals and Rocks, Their Origin, Form and Content. Vol. I. By F. Beyschlag, *et al.* 8vo. 542 pp. Price, $4.50. Macmillan, London.

Oils: Chemical Technology and Analysis of Oils, Fats and Waxes. Vol. 2. By Julius Isidor Lewkowitsch. 5th Ed. 8vo. 944 pp. Price, $6.50. The Macmillan Co., New York.

Petroleum: History and Romance of the Petroleum Industry. Vol. I. By J. D. Henry. 8vo. 320 pp. Price, $2.50. Author, London.

Poisons: Der chemische Giftnachweis. By C. Ipsen. 8vo. 79 pp. Price, $1.00. Wiesbaden.

Steel: Heat-treatment of Steel: a Comprehensive Treatise on Hardening, Tempering, Annealing Co. 8vo. 278 pp. Price, $2.50. Industrial Press, New York.

Ultraviolet Light: The Spectroscopy of the Extreme Ultraviolet. By Theodore Lyman. 8vo. 135 pp. Price, $1.50. Longmans, Green & Co., New York.

Ventilation: Heating and Ventilation Plants. By C. Lincoln Hubbard. 2nd Ed. 8vo. 300 pp. Price, $2.50. McGraw-Hill Book Co., New York.

RECENT JOURNAL ARTICLES

Air: Die desinfizierende Wirkung der Gasbeleuchtung auf Zimmerluft. By Knud Ahlborn. *Archiv für Hygiene*, Vol. 83, 1914, No. 3, pp. 155–86.

Air: Investigation of Sewer Air Following Boston Explosion. By H. W. Clark. *Engineering Record*, Vol. 70, 1914, No. 23, pp. 606–7.

Analysis: Gasanalytische Pipette, die ein Bewegen der Absorptionflussigkeit innerhalb der Pipette gestattet. By Georg Wempe. *Zeitschrift für angewandte Chemie*, Vol. 27, 1914, No. 86, pp. 584.

Blast Furnace: The Heat Balance of the Blast Furnace. By Sidney Cornell. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 12, pp. 747–50.

Blast Furnaces: Safety Regulations for Blast Furnaces. By F. H. Willcox. *The Iron Age*, Vol. 94, 1914, No. 22, pp. 1226–7.

Bleaching of Wool Fiber. By A. F. Musgrave. *Textile Colorist*, Vol. 36, 1914, No. 431, pp. 337–8.

Butter: The Effect of Renovation of Butter upon the Reichert-Meissl Number and Saponification Value. By F. O. Touney and F. W. Stockton. *American Journal of Public Health*, Vol. 4, 1914, No. 11, pp. 1083–5.

Carbide: Note on the Preparation of Pure Calcium Carbide. By M. Dekay Thompson. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 12, pp. 779–80.

Cement: Ueber die Verbindung $8CaO.Al_2O_3.2SiO_2$, der Hauptbestandteil (Alit) des Portlandzementklinders. By Ernst Jänecke. *Zeitschrift für anorganische Chemie*, Vol. 89, 1914, No. 4, pp. 355–69.

Cobalt: Ueber neue massanalytische Methoden zur Bestimmung von Kobalt neben Nickel. By Albert Metzl. *Zeitschrift für analytische Chemie*, Vol. 53, 1914, No. 9, pp. 537–41.

Copper Sulfide: Determination of Cuprous and Cupric Sulfide in Mixtures of One Another. By Eugen Posnjak. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 12, pp. 2475–9.

Cotton: The Preparation of Absorbent Cotton. By Jules Garcon. *Textile World Record*, Vol. 48, 1914, No. 2, pp. 76–8.

Dyes: Notes on Color Mixing and Possible Future Innovations and Economical Applications in the Same. By Raffaele Sansone. *Textile Colorist*, Vol. 36, 1914, No. 431, pp. 349–52.

Dyes: The Uses of Natural Dyestuffs. By Edward S. Chapin. *Textile Colorist*, Vol. 36, 1914, No. 431, pp. 329–31.

Electrolysis: Die Verarbeitung der bei der Elektrolyse der Kali-Endlangen Gewonnenen Stoffe. By Dietz. *Zeitschrift für angewandte Chemie*, Vol. 27, 1914, No. 84, pp. 569–72.

Engineers: The Engineer as a Factor in Modern Warfare. By Joseph E. Kuhn. *Engineering Record*, Vol. 70, 1914, No. 20, pp. 526–8.

Gas: An Electrical Process for Detarring Gas. By F. W. Steere. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 12, pp. 775–78.

Industry: Panic Economics and Emergency Problems with Especial Reference to the Present Industrial Situation. By F. A. Waldron. *The Journal of the American Society of Mechanical Engineers*, Vol. 36, 1914, No. 12, pp. 413–7.

Iron: A Cast Iron with Unusual Structure. By K. W. Zimmerscheid. *The Iron Age*, Vol. 94, 1914, No. 20, pp. 1120–3.

Iron: Concentration by the Goltra Process. By William R. Phillips. *The Iron Age*, Vol. 94, 1914, No. 20, pp. 1148–50.

Iron: Ueber eine empfindliche eisenreaktion und über eine, Methode zur kolorimetrischen Eisenbestimmung. By L. Tschngaeff and B. Orelkin. *Zeitschrift für anorganische Chemie*, Vol. 89, 1914, No. 4, pp. 401–4.

Light as a Factor of Efficiency. By W. A. D. Evans. *Textile World Record*, Vol. 48, 1914, No. 2, pp. 71–4.

Liquids: New Formulas for the Flow of Fluids in Pipes. By A. H. Anderson. *Engineering News*, Vol. 72, 1914, No. 22, pp. 1066–7.

Manganese: The Occurrence and Significance of Manganese in the Seed Coat of Various Seeds. By J. S. McHargue. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 12, pp. 2532–6.

Manganese: Ueber die quantitative Bestimmung des Mangans im Boden. By Bela von Horváth. *Zeitschrift für analytische Chemie*, Vol. 53, 1914, No. 9, pp. 581–93.

Photography: Some Recent Advances in Photography. By Henry Leffmann. *Journal of the Franklin Institute*, Vol. 178, 1914, No. 6, pp. 743–9.

Refrigeration: Insulating Materials Used in Refrigeration. By R. L. Shipman. *Refrigerating Work*, Vol. 48, 1914, No. 5, pp. 28–30.

Sanitation: Rational Basis for the Sanitation of Rivers and Harbors. By George A. Soper. *American Journal of Public Health*, Vol. 4, 1914, No. 11, pp. 1089–92.

Sewage: Shellfish Conservation and Sewage Disposal. By George A. Johnson. *American Journal of Public Health*, Vol. 4, 1914, No. 11, pp. 965–8.

Sewerage System for Panama-Pacific Exposition Grounds at San Francisco. By William C. Willard. *Engineering Record*, Vol. 70, 1914, No. 20, pp. 538–9.

Steel: Ultimate Strength of Carbon and Nickel-Steel Models of Quebec Bridge Members. Anonymous. *Engineering Record*, Vol. 70, 1914, No. 20, pp. 541–3.

Sugar: The Estimation of Cane Sugar and Lactose in Condensed Milk by Means of Acid Mercuric Nitrate. By Cecil Revis and George A. Payne. *The Analyst*, Vol. 39, 1914, No. 464, pp. 476–9.

Sugar: Versuche über die Loslichkeit und Kristallisationfähigkeit des Luchers in den Betriebssaften und Sirupablaufen. By H. Claassen. *Zeitschrift des Vereins der Deutschen Zucker-Industrie*, 1914, No. 705, pp. 807–841.

Tartaric Acid: Die quantitative Bestimmung der Weinsäure in Getränken und besonders in Weinen. By E. P. Häussler. *Zeitschrift für analytische Chemie*, Vol. 53, 1914, No. 9, pp. 542–61.

Water: A Qualitative Test for Water by the Use of the Acetylene-Cuprous Chloride Reaction. By E. R. Weaver. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 12, pp. 2462–8.

Water: Bacteriological Standards for Water on Common Carriers. Anonymous. *Engineering Record*, Vol. 70, 1914, No. 23, pp. 617–8.

Water: Beitrag zur Wasseranalyse: Schnelle Bestimmung des Magnesiums durch Titration bei Gegenwart von Calcium. By Victor Froboese. *Zeitschrift für anorganische Chemie*, Vol. 89, 1914, No. 4, pp. 370–6.

Water: Permutit und Polarit zur Wasserreinigung. By John Don. *Kolloid-Zeitschrift*, Vol. 15, 1914, No. 3, pp. 132–4.

Water: The Ultraviolet Rays and Their Application for the Sterilization of Water. By M. von Recklinghausen. *Journal of the Franklin Institute*, Vol. 178, 1914, No. 6, pp. 681–704.

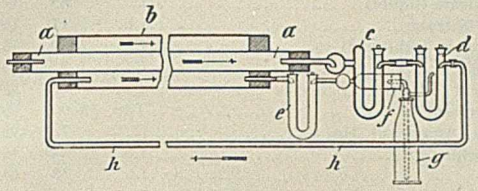
Water Softening and Decolorization. By W. A. Speery. *American Journal of Public Health*, Vol. 4, 1914, No. 11, pp. 1079–82.

Water-Works: Municipal Ownership and Operation of Water-Works. By M. N. Baker. *Engineering News*, Vol. 72, 1914, No. 23, pp. 1115.

RECENT INVENTIONS

By C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Apparatus for Use in Elementary Organic Analysis. H. Brach, Oct. 6, 1914. U. S. Pat. 1,112,432. In this apparatus a calcium chlorid tube, *c*, and a soda-lime tube, *d*, are connected in the usual manner to the combustion tube *a*. The escaping carbon monoxid and the carbonic acid which has not been absorbed, are returned through a connecting tube, *h*, to the front portion of the outer or jacket tube *b*, in order to be completely burned while passing therethrough and to be absorbed in the soda-lime tube *e* when escaping from the tube *b*; *f* is a straight calcium chlorid tube and *g* is a wash bottle charged with a solution of palladium chlorid in order to indicate the passage of the gas and the speed of the combustion.



Treating Mineral Oils. J. Dehnst, Oct. 6, 1914. U. S. Pat. 1,112,602. The unpleasant odor is removed from sulfur containing mineral oils by first adding sulfur to the oil and then distilling off the portions boiling at and below 150° C. The remaining oil is then heated to a temperature above 150° C. until the evolution of hydrogen sulfide has ceased.

Renewing Used Fullers' Earth. C. L. Parsons, Oct. 6, 1914. U. S. Pat. 1,112,650. Fullers' earth residues resulting from oil refining processes are restored to their original condition by treatment with a solvent of the oil treated in the refining process and a solvent of the coloring matter contained in the oil. These solvents are separated from the residues.

Barium Oxid. L. E. Saunders, Oct. 6, 1914. U. S. Pat. 1,112,721. Barium oxid is produced by decomposing barium sulfate by the heat of an electric arc maintained out of contact with the sulfate.

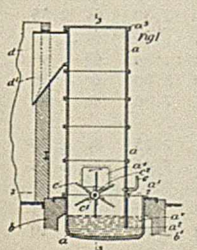
Alkali Cyanogen Compounds. J. C. Clancy, Oct. 6, 1914. U. S. Pat. 1,112,893. Calcium cyanamid and an alkali-metal sulfid are heated to a reacting temperature in the presence of carbonaceous material.

Converting Cast-Iron into Steel or Malleable Iron. J. A. Hunter, Oct. 6, 1914. U. S. Pat. 1,112,909. Cast-iron is heated to a high temperature but below its melting point and subjected at such temperature to the action of nitric acid.

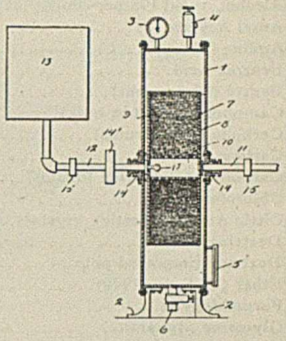
Improvement of Inferior-Grade Rubbers. D. Spence and W. F. Russell, Oct. 6, 1914. U. S. Pat. 1,112,938. Inferior grade rubber is subjected to the action of metallic sodium in the presence of moisture.

Hydrogen Production. C. Bosch and W. Wild, Oct. 6, 1914. U. S. Pat. 1,113,097. Hydrogen is produced by passing carbon monoxid and steam at a temperature between 350° C. and 650° C. over a catalytic agent in lumps containing more than 30 cobalt and a non-metallic, indifferent refractory and porous material.

Lead Oxid. W. Innes, Oct. 6, 1914. U. S. Pat. 1,113,123. Molten lead in the pot *a* is acted upon by the stirrer *c*, the blades of the stirrer dipping into the molten lead and throwing it upward to atomize it.



Lard Substitute. J. C. Chisholm, Oct. 6, 1914. U. S. Pat. 1,113,151. Oil to be hydrogenated and hydrogen are forced by centrifugal action outwardly through a porous drum formed of spirally wound wire or fine mesh wire gauze of catalytic material.



Varying the Velocity of Detonation of Explosives. C. A. Woodbury, Oct. 13, 1914. U. S. Pat. 1,113,275. The velocity of detonation of dynamite is controlled by utilizing large or small grains of ammonium nitrate. Where a relatively low velocity of detonation is desired, grains of ammonium nitrate of a relatively large size are employed.

Detinning Process. W. Savage, Oct. 13, 1914. U. S. Pat. 1,113,491. The scrap to be detinned is subjected to the action of a slime containing tin ammonium chlorid and gray tin. The slime transforms the white tin to be removed into non-adherent gray tin. The gray tin is transformed into white tin by melting.

Electrolyte for Use in Electro-Metallurgy. N. H. M. Dekker, Oct. 13, 1914. U. S. Pat. 1,113,546. An anode and a cathode are placed in an electrolyte consisting of a salt of the metal to be refined but no water except the water of crystallization of the salt and a current is passed through the electrolyte.

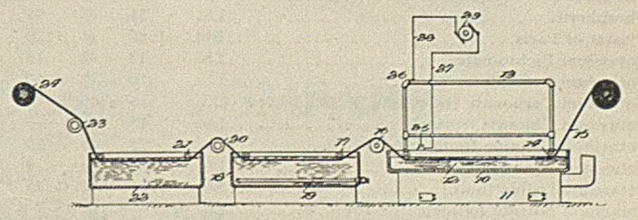
Caoutchouc Substances. F. Hofmann & C. Coutelle, Oct. 13, 1914. U. S. Pat. 1,113,630. The caoutchouc substance is produced by polymerizing isoprene in the presence of about 1 to 2 per cent of urea.

Colored Caoutchouc Substances. R. Ditman, Oct. 13, 1914. U. S. Pat. 1,113,759. The caoutchouc materials to be colored are treated with organic vat dyes and are then vulcanized by heating with sulfur at the vulcanization temperature.

Acetic Anhydrid. W. A. Beatty, Oct. 13, 1914. U. S. Pat. 1,113,927. Sulfuric anhydrid is mixed with carbon tetrachlorid and the products of the reaction are used to react upon sodium acetate.

Treatment of Oils, Fats, Etc. N. Testrup, Oct. 20, 1914. U. S. Pat. 1,114,067. Unsaturated organic bodies are hydrogenated by subjecting them in a state of minute sub-division to the action of hydrogen and a catalyzer.

Method for Cleaning Metals. A. A. Nelson, Oct. 20, 1914. U. S. Pat. 1,114,635. The iron or steel to be cleaned is first subjected to the action of an electric current as a cathode in a bath of a fused alkali metal salt, preferably sodium or potassium hydroxid, whereby a thin covering or surface film of the alkali metal is deposited upon the iron or steel. The iron or steel is then passed through a bath of hot water where the alkali metal film combines with the water with such violence as to remove rust, scale, oil or other impurities upon the surface of the metal.



MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF DECEMBER, 1914

ORGANIC CHEMICALS

Acetanilid	Lb.	31	@	33
Acetic Acid (28 per cent)	C.	1.75	@	2.00
Acetone (drums)	Lb.	17	@	20
Alcohol, denatured (180 proof)	Gal.	33	@	35
Alcohol, grain (188 proof)	Gal.	2.58	@	2.60
Alcohol, wood (95 per cent)	Gal.	45	@	47
Amyl Acetate	Gal.	2.75	@	—
Aniline Oil	Lb.	30	@	50
Benzoic Acid	Lb.	60	@	70
Benzol (90 per cent)	Gal.	34	@	35
Camphor (refined in bulk)	Lb.	44½	@	—
Carbolic Acid (drums)	Lb.	50	@	52
Carbon Bisulfide	Lb.	7	@	8
Carbon Tetrachloride (drums)	Lb.	12	@	—
Chloroform	Lb.	30	@	35
Citric Acid (domestic), crystals	Lb.	55	@	57
Dextrine (corn)	C.	2.77	@	3.02
Dextrine (imported potato)	Lb	—	@	—
Ether (U. S. P., 1900)	Lb.	15	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	21	@	21½
Oxalic Acid	Lb.	13	@	14
Pyrogallic Acid (bulk)	Lb.	1.90	@	2.10
Salicylic Acid	Lb.	67½	@	70
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	1.99	@	2.20
Starch (potato)	Lb.	—	@	—
Starch (rice)	Lb.	—	@	—
Starch (sago)	Lb.	—	@	—
Starch (wheat)	Lb.	5	@	10
Tannic Acid (commercial)	Lb.	60	@	66
Tartaric Acid, crystals	Lb.	43	@	44

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7¼	@	7½
Acetate of Lime (gray)	C.	2.00	@	2.05
Alum (lump)	C.	2.75	@	3.00
Aluminum Sulfate (high-grade)	C.	1.10	@	1.50
Ammonium Carbonate, (domestic)	Lb.	8¼	@	9
Ammonium Chloride, (gray)	Lb.	6¼	@	6¾
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic (white)	Lb.	4½	@	6
Barium Chloride	Ton	50.00	@	60.00
Barium Nitrate	Lb.	15	@	16
Barytes (prime white, foreign)	Ton	19.00	@	25.00
Bleaching Powder (35 per cent)	C.	1.37½	@	2.00
Blue Vitriol	C.	4.35	@	4.55
Borax, crystals (bags)	Lb.	3¾	@	4½
Boric Acid, crystals (powd.)	Lb.	7	@	8
Brimstone (crude, domestic)	Long Ton	22.00	@	22.50
Bromine (bulk)	Lb.	40	@	50
Calcium Chloride (lump)	Ton	11.70	@	12.00
Chalk (light precipitated)	Lb.	4½	@	5½
China Clay (imported)	Ton	14.00	@	16.00
Feldspar	Ton	8.00	@	14.00
Fuller's Earth (powdered, foreign)	C.	80	@	90
Green Vitriol (bulk)	C.	30	@	32
Hydrochloric Acid (18°)	C.	1.15	@	1.65
Iodine (resublimed)	Lb.	3.75	@	4.00
Lead Nitrate	Lb.	8	@	8⅛
Litharge (American)	Lb.	5	@	5¼
Lithium Carbonate	Lb.	1.00	@	1.10
Magnesium Carbonate	Lb.	4¼	@	5¼
Magnesite "Calcined"	Ton	40.00	@	50.00
Nitric Acid (36°)	Lb.	3⅞	@	4¼
Phosphoric Acid (sp. gr. 1.75)	Lb.	28	@	28½
Phosphorus	Lb.	35	@	95
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate	Lb.	12	@	14
Potassium Bromide	Lb.	70	@	80
Potassium Carbonate (calcined), 80 @ 85%	C.	5½	@	6
Potassium Chlorate, crystals	Lb.	15	@	—
Potassium Cyanide (bulk), 98–99%	Lb.	25	@	30
Potassium Hydroxide	Lb.	8	@	9
Potassium Iodide (bulk)	Lb.	3.15	@	3.25
Potassium Nitrate (crude)	Lb.	—	@	—
Potassium Permanganate (bulk)	Lb.	15	@	20
Quicksilver, Flask (75 lbs.)		51.00	@	54.00
Red Lead (American)	Lb.	5½	@	6
Salt Cake (glass makers')	C.	55	@	65
Silver Nitrate	Oz.	31½	@	32¾
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash (48 per cent)	C.	67½	@	72½
Sodium Acetate	Lb.	5	@	7
Sodium Bicarbonate (domestic)	C.	1.00	@	1.10
Sodium Bicarbonate (English)	Lb.	3½	@	4
Sodium Bichromate	Lb.	4¾	@	5
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	14	@	—
Sodium Hydroxide (60 per cent)	C.	1.55	@	1.57½
Sodium Hyposulfite	C.	1.60	@	1.90
Sodium Nitrate (95 per cent, spot)	C.	1.85	@	1.90
Sodium Silicate (liquid)	C.	85	@	1.15
Strontium Nitrate	Lb.	15	@	17
Sulfur, Flowers (sublimed)	C.	2.20	@	2.60
Sulfur, Roll	C.	1.85	@	2.15
Sulfuric 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.	9¾	@	10
Tin Oxide	Lb.	38	@	40
White Lead (American, dry)	Lb.	5	@	5¼
Zinc Carbonate	Lb.	8¼	@	8¾
Zinc Chloride (granulated)	Lb.	4½	@	5
Zinc Oxide (American process)	Lb.	5⅜	@	6⅜
Zinc Sulfate	C.	2.35	@	2.70

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	45	@	57
Black Mineral Oil, 29 gravity	Gal.	12½	@	13
Castor Oil (No. 3)	Lb.	8¼	@	9
Ceresin (yellow)	Lb.	10	@	25
Corn Oil	C.	5.70	@	5.75
Cottonseed Oil (crude). f. o. b. mill	Gal.	36	@	36½
Cottonseed Oil (p. s. y.)	Lb.	5½	@	6
Cylinder Oil (light, filtered)	Gal.	20	@	25
Japan Wax	Lb.	10	@	11
Lard Oil (prime winter)	Gal.	90	@	92
Linseed Oil (raw)	Gal.	45	@	—
Menhaden Oil (crude)	Gal.	33	@	—
Naphtha, 68 @ 72°	drums	—	@	17
Neatsfoot Oil (20°)	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.)	Lb.	3⅛	@	3¼
Paraffine Oil (high viscosity)	Gal.	26	@	27
Rosin ("F" grade) (280 lbs.)	Bbl.	3.80	@	3.90
Rosin Oil (first run)	Gal.	25	@	—
Shellac, T. N	Lb.	14	@	14½
Spermaceti (cake)	Lb.	28	@	30
Sperm Oil (bleached winter), 38°	Gal.	70	@	71
Spindle Oil, No. 200	Gal.	17	@	18
Stearic Acid (double-pressed)	Lb.	9	@	11
Tallow (acidless)	Gal.	62	@	63
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	46	@	46½

METALS

Aluminum (No. 1 ingots)	Lb.	18½	@	19
Antimony (Hallet's)	Lb.	14½	@	15½
Bismuth (New York)	Lb.	2.80	@	2.90
Bronze powder	Lb.	—	@	—
Copper (electrolytic)	C.	13⅛	@	13¼
Copper (lake)	C.	13¼	@	13⅜
Lead, N. Y	C.	3.80		
Nickel	Lb.	—	@	—
Platinum (refined)	Oz.	50.00	@	52.00
Silver	Oz.	48½	@	50
Tin	C.	33.75	@	33.87½
Zinc	C.	5.60	@	5.65

FERTILIZER MATERIALS

Ammonium Sulfate	C.	2.55	@	2.62½
Blood (dried)	Unit	2.80	@	2.90
Bone, 4½ and 50 (ground, raw)	Ton	30.00	@	—
Calcium Cyanamid	Unit of Ammonia	2.30	@	2.35
Calcium Nitrate (Norwegian)	C.	—	@	—
Castor meal	Unit	—	@	—
Fish Scrap (domestic, dried)	Unit	3.00	&	10
Phosphate, acid (16 per cent bulk)	Ton	7.00	@	—
Phosphate rock; f. o. b. mine:				
Florida land pebble (68 per cent)	Ton	2.25	@	2.50
Tennessee (70–80 per cent)	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent	Ton	nominal		
Pyrites (furnace size, imported)	Unit	13	@	—
Tankage (high-grade)	Unit	2.80	&	10