

The Journal of INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society



Editor: CHAS. H. HERTY

Assistant Editor: LOIS W. WOODFORD

Advisory Board: H. E. BARNARD
CHAS. L. REESE

J. W. BECKMAN
GEO. D. ROSENGARTEN

A. D. LITTLE
T. B. WAGNER

A. V. H. MORY

EDITORIAL OFFICES:

One Madison Avenue, Room 343
New York City
TELEPHONE: Gramercy 0613-0614

ADVERTISING DEPARTMENT:

170 Metropolitan Tower
New York City
TELEPHONE: Gramercy 3880

Cable Address: JIECHEM

Volume 13

APRIL 1, 1921

No. 4

CONTENTS

EDITORIALS:

On to Rochester.....	282
Echoes from the 66th Congress.....	282
Specific Facts.....	283
Death of Lord Moulton.....	284

THE CHEMICAL INDUSTRY AND TRADE OF SWITZERLAND.
O. P. Hopkins.....

285

ORIGINAL PAPERS:

An Application of the Vapor Pressures of Potassium Compounds to the Study of the Recovery of Potash by Volatilization. Daniel D. Jackson and Jerome J. Morgan.....	292
Possible Uses of Corncob Cellulose in the Explosives Industry. L. G. Marsh.....	296
Some Interpretations of the Ammonia Synthesis Equilibrium. R. S. Tour.....	298
The Production of Artificially Dense Charcoal. L. F. Hawley.....	301
The Melting Point of Ammonium Sulfate. James Kendall and Arthur W. Davidson.....	303
Rapid Dry Combustion Method for the Simultaneous Determination of Soil Organic Matter and Organic Carbon. J. W. Read.....	305
Studies on the Nitrotoluenes. VI—The Three-Component System: <i>o</i> -Nitrotoluene, <i>p</i> -Nitrotoluene, 1,2,4-Dinitrotoluene. James M. Bell and Edward B. Cordon.....	307
Studies on the Nitrotoluenes. VII—The Three-Component System: <i>p</i> -Nitrotoluene, <i>o</i> -Nitrotoluene, 1,2,4,6-Trinitrotoluene. James M. Bell and Fletcher H. Spry.....	308
The Anilides of β -Oxynaphthoic Acid. E. R. Bruns-kill.....	309
The Non-Biological Oxidation of Elementary Sulfur in Quartz Media. W. H. MacIntire, F. J. Gray and W. M. Shaw.....	310
The Melting Point of Diphenylamine. Homer Rogers, W. C. Holmes and W. L. Lindsay.....	314
The Activity of Phytase as Determined by the Specific Conductivity of Phytin-Phytase Solutions. F. A. Collatz and C. H. Bailey.....	317
Studies of Wheat Flour Grades. I—Electrical Conductivity of Water Extracts. C. H. Bailey and F. A. Collatz.....	319

The Rate of Evaporation of Ethyl Chloride from Oils. Charles Baskerville and Myron Hirsh.....	322
Boron in Relation to the Fertilizer Industry. J. E. Breckenridge.....	324
Determination of Chlorides in Petroleum. Ralph R. Matthews.....	325

LABORATORY AND PLANT:

Humidity Control by Means of Sulfuric Acid Solutions, with Critical Compilation of Vapor Pressure Data. Robert E. Wilson.....	326
Notes on Laboratory and Demonstration Apparatus. Clifford D. Carpenter.....	332
Solvents for Phosgene. Charles Baskerville and P. W. Cohen.....	333

ADDRESSES AND CONTRIBUTED ARTICLES:

Studies on the Chemistry of Cellulose. I—The Constitution of Cellulose. Harold Hibbert.....	334
Combustion Smokes. Geo. A. Richter.....	343

RESEARCH PROBLEMS IN COLLOID CHEMISTRY. Wilder D. Bancroft.....

346

SCIENTIFIC SOCIETIES:

Rochester Ready for Chemical Cohorts; Philadelphia College of Pharmacy Celebrates One Hundredth Anniversary; New York Chemists' Club Confers Honorary Membership; Colloid Development; Calendar of Meetings.....	352
--	-----

NOTES AND CORRESPONDENCE:

Note on the Use of Potassium Permanganate in the Determination of Nitrogen by the Kjeldahl Method; The Formation of Anthracene from Ethylene and Benzene—Correction; The Estimation of Cellulose in Wood; Phthalic Anhydride Derivatives; A Memorial of Sir William Ramsay.....	358
---	-----

WASHINGTON LETTER.....	364
LONDON LETTER.....	365
PARIS LETTER.....	366
INDUSTRIAL NOTES.....	367
PERSONAL NOTES.....	368
GOVERNMENT PUBLICATIONS.....	369
BOOK REVIEWS.....	372
NEW PUBLICATIONS.....	374
MARKET REPORT.....	375

EDITORIALS

On to Rochester!

Those who attended the meeting of the AMERICAN CHEMICAL SOCIETY at Rochester in 1913 have carried with them constantly memories of a delightful week of intellectual stimulation and charming hospitality. That opportunity is soon to present itself again, for the 1921 Spring Meeting will be held during the week of April 25 to 29, with the Rochester Section acting as host.

During the intervening eight years that Section has increased largely in numbers and has justly earned the reputation of being one of the most flourishing of our Local Sections. Its members are determined to add fresh laurels to the record of 1913 by providing a program of scientific and social activities which insures a memorable meeting.

It is particularly appropriate that those attending are to have the pleasure of learning to know personally Senator James W. Wadsworth, Jr., and Congressman Nicholas Longworth, for each of these distinguished members of Congress has heartily worked for legislation affecting chemistry. Then, too, a treat awaits us in the public address of that venerable youth, Dr. Charles F. Chandler.

Even the railroads have given things a boost by offering round trip rates at one fare and a half on the certificate plan. (See preliminary program for details.)

Times are quiet in a business way. Let's take advantage of the opportunity to assemble for common counsel in preparation for the active days which all are confident lie just ahead.

Echoes from the 66th Congress

The 66th Congress has adjourned, *sine die*. Looking back over its history a remarkable picture presents itself. With Republican majorities in both Senate and House, that Congress stood logically committed to the policy of protection of home industries. At its initial session bills were introduced whose object was the effective safeguarding of a number of chemical and allied industries—dyes, chemical glassware and porcelain, scientific instruments, potash, magnesite, tungsten, etc. As the work of the Congress developed it was plainly evident that the prevailing sentiment was strongly in favor of these bills, yet not one of them was enacted into law. We missed our guess; the Senate didn't pass the dye bill.

The unceasing opposition of Senators Moses and Thomas to the dye bill has been discussed in these columns at length; Senator Penrose frankly and publicly announced his opposition to the whole group of bills on the ground that they were "pop gun bills." However, the record of Senator Penrose on the farmers' emergency tariff bill suggests that in the 67th Congress he owes very active and vigorous support of protective measures for the chemical and allied industries if he believes in protection as a matter of principle rather than of policy, and we believe he does.

The failure of one other measure must bring regret to all interested in our industrial development, namely, the bill providing relief for the Patent Office. Here, again, was a case where a great majority favored the legislation, but the bill was strangled by a rider which incorporated the feature of giving to the Federal Trade Commission the right to receive assignments of patents, and the power to administer them, including the regulation of royalties. The AMERICAN CHEMICAL SOCIETY protested in vain against this doubling up. The Senate refused to adopt the report of the Conference Committee and the Patent Office is still without relief.

In the next Congress these bills bearing on patent questions will again be introduced, presumably as separate bills. If so, the bill giving the Federal Trade Commission, or any other governmental agency, the powers above referred to should be vigorously opposed; for it is contrary to the spirit of the times, it will result in the gradual accumulation of two distinct classes of patents—the one owned by individuals, the other by the government, and in legislation over conflicting patents endless confusion will be brought, stimulation of individual invention will be handicapped, and the public, which is the ultimate beneficiary under the whole idea of our patent system, will be the loser.

There will be no difference of opinion about a bill providing for the relief of the Patent Office. The crippling of its staff during past years and the steady decrease in the efficiency of the service it can render appeal to all as justifying a prompt remedy. The difficulties just experienced in getting this relief suggest that still more fundamental legislation in its behalf should be enacted. At present the Patent Office occupies an anomalous position; it is a subdivision of an executive department, whereas its functions are purely judicial. An appeal from the decision of the Commissioner of Patents does not go to the Secretary of the Interior Department, but to the courts. The salary of the Commissioner is now determined by that prevailing for bureau chiefs, whereas the Commissioner should be essentially a man of judicial training, receiving the higher salary comparable with that of other judges. From the fees paid in past years, which go direct to the Treasury of the United States, approximately \$8,000,000 more has been received than has been expended by Congressional appropriation on the Patent Office. Why should the patentee of a new chemical process or compound pay fees to the Government to aid in maintaining the marines in Haiti or decreasing the postal deficit, while he is unable to secure desired copies or reproductions of foreign chemical patents because the Congressional appropriation for that purpose is exhausted?

Applicants for patents desire service, the best service obtainable. They are willing to pay for it. If necessary let the fees be increased, but let them go direct to the maintenance of the Patent Office at the highest possible state of efficiency.

Specific Facts

Much has been said, much has been written within the last two years about the use of the dye plants of Germany as the source of her supply of poison gas during the war. The significance of this fact has not yet been grasped by the average citizen. We believe this is due to the use of only general terms in discussing the matter. Specific information seems to be required to drive the thought home. For this reason, there is reproduced here a most illuminating document.¹

Report of the British Mission Appointed to Visit Enemy Chemical Factories in the Occupied Zone Engaged in the Production of Munitions of War

Members of the British Mission:

Brig. Gen. H. Hartley, C. O. W. D.
Mr. F. H. Carr.
Capt. A. C. G. Egerton.
Lieut. H. G. Greenwood.
Dr. H. Levenstein.
Mr. W. Macnab.
Mr. A. W. Tangye.
Mr. S. I. Levy, Secretary.

Delegates of allied Governments who accompanied the mission in the British zone:

American—

Lieut. Col. C. W. Steese, O. D., U. S. Army.
Lieut. Col. J. F. Norris, C. W. S., U. S. Army.
Maj. T. W. Sill, C. W. S., U. S. Army.
Capt. R. D. McGrath, C. W. S., U. S. Army.
Capt. J. W. Martin, Ord., U. S. Army.
Lieut. H. J. Himmelein, R. D., U. S. Army.

French—

Col. M. Marquayrol (direction des Poudres).
Comm. M. Chaud.
Mons. T. Sordes.
Mons. N. Simon.

Italian—

Capt. C. Mazetti.
Lieut. I. Cardoso.
Lieut. M. Malvano.
Sig. M. Bonelli.
Sig. M. Piersel.

Belgian—

Capt. M. Janlet.

The usual procedure was first to have a general view of a factory in order to get an idea of its lay-out and prewar capacity, and of the way in which this had been utilized and extended for war purposes. Afterwards the mission divided into three sections in order to get details of the war productions, as follows:

Initial products (e. g., sulphuric acid, nitric acid, ammonia, chlorine, caustic soda): Mr. Tangye, Lieut. Greenwood, Capt. Egerton.

Explosives: Mr. Macnab, Mr. Levy.

Poison gas: Mr. Levinstein, Mr. Carr.

The information obtained by each section has been embodied in the present report.

In some cases considerable difficulty was experienced in obtaining accurate details of manufacture, especially as regards substances which have a peace value, and the information must be accepted with some reserve on this account, although it was checked by cross-examination of the officials concerned and by a careful examination of the plant admittedly employed for war purposes.

As a result of its visit, the mission had obtained valuable information as to the methods of manufacture of explosives and poison gases employed by the enemy, and of the initial products necessary for their production. It was also able to form a clear impression of the military value of the German chemical industry.

Some years before the war, a combination was formed by the Bayer, Badische and A. G. F. A. companies and somewhat later a second group was formed which included Meister Lucius &

Bruning, Casella & Kalle. During the war, these two groups amalgamated, and the Griesheim Elektron, Weiler ter Meer, Leonhardt, and other smaller companies, entered the combination, which is known as the I. G. It was largely owing to the efforts of this combination that Germany was enabled to continue the war in spite of the blockade. The I. G. works produced the bulk of the synthetic ammonia and nitric acid needed for the production of fertilizers and explosives, all the poison gas (with the exception of some chlorine and phosgene), and a large proportion of the high explosives.

The following are the more important works of the I. G. which were not visited, as they are outside the occupied zone:

Factories of the Aktien Gesellschaft für Anilinfabrikation.
Factories of the Griesheim Elektron Gesellschaft.
Factory of the Bayer Co. at Elberfeld.
Factory of the Badische Co. at Merseburg.
Factory of Casella & Co., Mainkur, near Frankfurt.
Factory of Leonhardt & Co., Mulheim, near Frankfurt.

A summary of the information obtained as to the war production of the factories visited is given under the headings of "Initial products," "Explosives and poison gases."

INITIAL PRODUCTS FOR MANUFACTURE OF EXPLOSIVES AND POISON GAS.

The principal materials concerned are ammonia, nitric acid, sulphuric acid, and chlorine, and it was on the output of these that the war production of chemical munitions depended. The expansion of output by the factories of the I. G. combination during the war is shown by the following tables:

Ammonia (metric tons NH ₃ per day).			
	1914	1918	
Oppau.....	25	250	
Merseburg.....	(1)	400	
Total.....	25	650	
1 Nil.			

Nitric acid (metric tons 100 per cent acid per day).			
	1914	1918	
Leverkusen.....	56	180	
Höchst.....	150	375	
Oppau.....	?	100	
Ludwigshafen.....	40 (?)	40	
Weiler ter Meer.....	12	24	
Total.....	258	719	

Oppau has the power to produce now 500 tons HNO₃ daily, still retaining sufficient ammonia to supply the output at Höchst.

Sulphuric acid (metric tons 100 per cent acid per day).			
	1914	1918	
Leverkusen.....	340	470	
Höchst.....	224	280	
Ludwigshafen.....	275	410	
Weiler ter Meer.....	48	60	
Total.....	887	1220	

Meister Lucius & Bruning have also erected a large new plant at Höchst which has not yet started and was not examined.

The Bayer Co. has erected at Dormagen a large vitriol plant equal to 250 tons per day.

Chlorine (metric tons per day).			
	1914	1918	
Leverkusen.....	7	20	
Höchst.....	4	8	
Ludwigshafen.....	13	35	
Total.....	37	63	

Explosives.—No arrangements appear to have been made prior to the outbreak of war to utilize the resources of any of the dye factories for war purposes, and on mobilization their chemists were called up for military service. After the battle of the Marne the Government realized the need for expanding the output of explosives and most of the chemical works were producing small quantities by the end of 1914. The demands made on them increased during 1915, but it was not until 1916 that plant was laid down to assist in the enormous production of explosives required by the Hindenburg program. Most of the big extensions of the synthetic ammonia and of the nitric and sulphuric acid plants date from this time, many chemists being released from the army and the scientific staff of some of the works being augmented. Standardized plant used for the manufacture of dyes was converted for the production of explosives with remarkable speed; for instance, at Leverkusen a T. N. T. plant producing 250 tons per month was put into operation in six weeks.

¹ Reprinted from the Hearings before the Committee on Ways and Means, House of Representatives, on H. R. 2706 (the original number of the Longworth bill for the protection of the coal-tar chemical industry), pages 210-214.

The following table shows the amounts produced in the factories visited:

High explosives and intermediates.

Quantities of intermediates are shown only where these were not converted to finished explosives in the producing works.

[Metric tons per week.]

Factory	Ammonium nitrate.	Dinitrobenzene.	Dinitrotoluene.	Tritnitrotoluene.	Monitronaphthalene.	Dinitronaphthalene.	Dinitrochlorobenzene.	Dinitrophenol.	Picric acid.	Tritnitroanisole.	Dinitrodiphenylamine.	Hexanitrodiphenamine.
Leverkusen...	250	250	...	150	40	31
Domagen...	600
Ürdingen...	60	75	(2)
Höchst...	500	140	...	200	30	...	1½
Ludwigshafen...	...	25	50	15	300	35	25½	...
Oppau...	200
Merseburg...	(?)
Wiesdorf...	120
Schlebusch...	100	...	150

¹ For 3 months only.

² Small.

³ For 1 year.

Other intermediates—Ludwigshafen, sodium benzene sulphonate, 100 tons per week.

Other explosives—Schlebusch, hexanitrodiphenylsulphide, 15 tons per week.

Poison gas.—At first chlorine and phosgene were the main requirements, but afterwards a variety of organic substances were employed, all of which were made by the factories of the I. G. combination. Many of these substances were new and difficult to prepare, and rapid production was only possible owing to the speed with which the peace organization of the dye factories could be utilized for this purpose. When the Government wished to introduce a new gas, a conference of the various firms was held at Berlin to determine how the manufacture should be subdivided in order to use existing plants to the best advantage. For instance, the initial stages of the manufacture of mustard gas were carried out at Ludwigshafen and the final stage at Leverkusen.

The following table shows the production of gas and intermediate products in the various factories visited:

Propellant explosives, detonating substances, etc.

[Metric tons per week.]

Factory	Nitro-cellulose powder.	Di-ethyl phenyl urea.	Di-phenyl amine.	Nitro-glycerine.	Cor-dite paste.	Dyna-mite.	Tet-ryl.	Ful-min-ate.	Lead azide.
Ürdingen...	35	7
Kuppersteg...	0.7
Troisdorf...	250	21	40	...	6	7	0.7
Schlebusch...
Opladen...	35	75
Wiesdorf...	(?)50	40

Output of finished poison gases from various works.

Factory	Monthly output (metric tons).		Total production (if known).	Date of commencement.
	Average.	Maximum.		
1. Chlorine...	Leverkusen 600	Prior to war.
	Höchst 240	Do.
	Ludwigshafen 860	1,261	38,600	Do.
2. Phosgene...	Leverkusen...	30	...	Do.
	Ludwigshafen 288	621	10,682	Do.
3. Diphosgene...	Leverkusen...	300	...	June, 1915.
	Höchst 139	268	3,616	September, 1916.
4. Chlorpicrin...	Leverkusen...	200	...	July, 1916.
	Höchst 45	101	1,127	August, 1916.
5. Xylol bromide....	Leverkusen...	60	...	March, 1915.
6. Bromacetone	do	20	...	July, 1916.
7. Brom acetone, brom-ethylmethylketone....	Höchst	19	45	685 April, 1915.
8. Phenyl carb-ylamine chloride...	do	65	124	721 March, 1917.
9. Mustard gas.	Leverkusen...	300	4,500	Before July, 1917.
10. Diphenyl-chlor arsine	Höchst	150	300	3,000 May, 1917.
Diphenyl-cyano arsine....	do	February, 1918.
11. Ethyldichlor arsine....	do	78	150	1,092 August, 1917.
12. Dichlor-methyl....	do	26	51	233 September, 1917.
13. Dibrom-methyl ether....	do	7	29	69 April, 1917.

¹ Estimated from capacity of plant. Probably the same quantity was produced at some other factory as the output of thiodiglycol from Ludwigshafen would suffice for this.

Output of Intermediate Products for Poison Gas Manufacture.

Finished gas.	Intermediate products.	Total output (metric tons).	Place of production.	Destination of intermediate products.
Phenylcarbamylamine...	Phenyl mustard oil	(1) 7,026	Kalle	Höchst.
Mustard gas.....	Thiodiglycol	...	Ludwigshafen	Leverkusen and 1 other factory.
Diphenylchlorarsine.	Phenyl arsenic acid	1,600	do.	Unknown.
	Diphenylarsenic acid	1,200	Kalle	Do.
		4,800	Leverkusen	Probably A. G. F. A., Berlin.
Ethyldichlorarsine...	Ethyl arsenious oxide	840	Ludwigshafen	Höchst.

¹ Not obtained.

NOTE.—In addition Höchst produced 3,000 tons of diphenyl chlor- and cyanarsines from own intermediates.

MILITARY IMPORTANCE OF THE GERMAN CHEMICAL INDUSTRY.

The above figures for the output of explosives and gas show the great military value of the factories of the I. G. combination. Although no arrangements had been made to mobilize them at the outbreak of hostilities, they were rapidly converted to war purposes, thanks to their highly trained personnel and the great technical resources of their peace organization. In the future it is clear that every chemical factory must be regarded as a potential arsenal, and other nations can not therefore submit to the domination of certain sections of chemical industry which Germany exercised before the war. For military security it is essential that each country should have its chemical industry firmly established, and this must be secured as one of the conditions of peace, as otherwise we are leaving Germany in possession of a weapon which will be a permanent menace to the peace of the world.

The key to Germany's war production of explosives was the Haber process for the production of ammonia from atmospheric nitrogen. It is significant that large scale production by this process only began at the end of 1912, and that in the early part of 1914 great pressure was put on the Badische Co. to increase its output. During the war, owing to the extension of the Haber plants at Oppau and Merseburg, Germany has become independent of foreign countries for her supplies of ammonia and nitric acid, substances indispensable for the manufacture not only of high explosives but also of fertilizers for food production. Without such a process Germany could not have made the nitric acid required for her explosives programme, nor obtained fertilizers for food production after the supply of Chile salt-peter had been stopped by our blockade, and it is probable that she could not have continued the war after 1916. In the event of another war we might be cut off from supplies of salt-peter.

The resources of the German dye industry are of no less military importance. Most of the gases employed toward the end of the war were complex organic substances, none of which had been made previously except in small quantities, and some of which were prepared for the first time during the war. Gas warfare will undoubtedly continue to develop in this direction, and in the future organic substances will be employed which we do not know to-day. The use of gas will always offer great opportunities for surprise in military operations, and the experiences of the present war has shown that rapid production of a new gas is essential if the surprise is to be effective. Any country without a well-developed organic chemical industry will be severely handicapped in this respect.

H. HARTLEY,

Brigadier General,

On Behalf of the Members of the Mission.

LONDON, February 26, 1919.

Death of Lord Moulton

On March 9, 1921, Lord Moulton, the head of British Dyes, Ltd., and President of the Association of British Chemical Manufacturers, died suddenly at his residence, Onslow Square, London. Throughout the critical war period he performed an inestimable public service through his work as Chairman of the Advisory Committee on Chemical Products and the Committee on High Explosives. After the war his talents were unselfishly and intensely devoted to the permanent establishment of the British dye industry. His guiding principle was the gospel of "work and still more work."

THE CHEMICAL INDUSTRY AND TRADE OF SWITZERLAND

By O. P. Hopkins

1824 BELMONT ROAD, WASHINGTON, D. C.

The war placed Switzerland in a most trying and delicate position. Always in danger of being forced into the conflict, she found herself hard pressed for favors from both sides, and equally hard pressed to find sufficient food and fuel for her own people. Some industries, especially those engaged on luxuries, suffered from foreign import restrictions, while the great textile industry was deprived of raw materials by foreign export restrictions. She is alive to tell the tale, however, and in most ways better off than her belligerent neighbors. A number of her industries were helped by the war. The high price of her money is at once an indication of her economic strength and a handicap in the marketing of her goods. Nine-tenths of the pessimism in Swiss trade is based on this exchange difficulty.

Although the majority of the inhabitants are engaged in agricultural pursuits, Switzerland is known abroad for its manufacturing industries, the products of which are largely exported, whereas agriculture supplies only a part of the country's needs. These industries are unique in that they depend almost wholly upon imported raw materials. The more valuable exports in normal times are embroideries and cotton goods, silk goods, watches and clocks, machinery, ready-made clothing, timber, woolen goods, chemicals, cheese, condensed milk, and chocolate. Swiss milk is used in the manufacture of cheese, condensed milk, and chocolate, some of the chemicals are based upon domestic supplies of salt, lime, and asphalt, and the timber is home grown, but the great bulk of manufactured goods is made entirely of imported materials. They are mainly highly finished goods that sell on a quality basis in the most competitive markets. All of which is a tribute to the skill of the Swiss workman, the excellence of the country's technical training, and the intelligence of the Swiss manufacturer.

Whatever may have been the effects of the war on other industries, there is no disputing the fact that the chemical industries as a whole were benefited, particularly the dye and electrochemical branches. According to the census of 1911, there were at that time 197 enterprises engaged in the manufacture of chemicals, employing 8692 workers. In 1918 there were 270 concerns, employing 17,764 workers. Before the war the exports of chemicals (nearly 90 per cent of the production is exported) were roughly valued at \$20,000,000, about one-fourth of which were dyes. During the first six months of 1920 the value of chemical exports reached the imposing total of \$30,000,000, of which more than two-thirds were dyes. (These are chemicals in the stricter sense of the word and do not include many allied products.) Whereas the chemical exports ranked about ninth before the war, they now rank third, judging from the incomplete 1920 returns.

THE DYE INDUSTRY

Coal-tar dyes were manufactured at an early date

in Switzerland, and a fair share of the credit for the development of this industry is not always given the Swiss chemist. The early and successful start is usually attributed to the excellent technical training afforded, to the steady domestic demand for high-class colors, and to the fact that no patent laws affecting chemicals were in force in Switzerland previous to 1908, a circumstance favoring the use of foreign patents without restriction. At any rate, the production of the best class of dyes increased steadily until an export trade of more than \$5,000,000 was recorded in 1913, the year before the war began. As far back as 1896 the exports were valued at \$2,600,000. It is understood that the exports amount to more than 80 per cent of the production and that the lower-priced staple dyes do not figure prominently in the trade.

When the German dyes were excluded from the world markets the Swiss makers found it impossible to meet the demands made upon them. They were not able to maintain their pre-war exports so far as quantity was concerned, as there were difficulties in getting supplies of intermediates and also difficulties in delivering the finished products. But prices rose rapidly and the makers profited. Previous to the war the industry relied largely upon intermediates from Germany, but these supplies were cut off, and the dye plants were obliged to undertake the manufacture of intermediates from crudes supplied by Austria, England, Germany, France, and even the United States, a very close coöperation being worked out with the English for an exchange of crudes for finished dyes.

The demand did not fall off when hostilities ceased, the productive capacity has been greatly increased since that time, and the deliveries of raw materials have been satisfactory, so that the value of the export trade has reached a rather remarkable figure. In 1918, the last year of the war, the value of exports was given as \$18,900,000. In 1919 the value had risen to \$26,000,000, although the quantity was still slightly below the figure for 1913. Figures for the full year 1920 are not available, but estimating the total at twice the value of the exports for the first six months, we arrive at the impressive sum of \$44,500,000. The quantity exported, estimated in the same manner, was 25,977,000 lbs., an increase of 8,107,000 lbs. over 1919 and of 6,518,000 lbs. over 1913. The development of the export trade in dyes has been as follows:

YEAR	QUANTITY Pounds	VALUE
1896.....	5,417,000	\$2,700,000
1913.....	19,459,000	5,500,000
1918.....	12,939,000	18,900,000
1919.....	17,870,000	26,000,000
1920.....	25,977,000 ¹	44,500,000 ¹

¹ Twice the total for the first six months.

The increasing activity of the Swiss exporters has caused no little discussion in this country. It is felt by some that German dyes and Swiss dyes made from German or Austrian materials are coming in

from Switzerland that would be excluded by the War Trade Board if properly described. It is rather difficult to get at the facts. That no coal is mined in Switzerland is well known. Facilities for the distillation of coal tar recovered at gas plants have recently been created, but no statistics of production are available. The bulk of the crudes are imported, and some of the intermediates. In 1919, under the heading of aniline, aniline oil, and aniline compounds for the manufacture of dyes, the total imports were only 1,756,000 lbs., of which 84 per cent were from England, 9 per cent from Germany, and smaller percentages from France and the United States. (These statistics are from official Swiss returns, which are considered reliable.) In 1918, a war year, about 4,000,000 lbs. were imported, of which only 7000 lbs. were attributed to Germany. The imports of aniline intermediates for the first six months of 1920 were much heavier, however—4,600,000 lbs., or at the rate of more than 9,000,000 lbs. for the year. Germany's share for the first six months was 172,620 lbs.

But the Swiss dye makers now rely largely upon crudes rather than upon intermediates, and the statistics show that in 1919 the imports of such crudes, given as "coal-tar derivatives for the manufacture of dyes" in the Swiss statistics,¹ amounted to 5,291,000 lbs., of which England supplied 29, France 28, Germany 27, Austria 15, and the United States about 1 per cent. It is obvious, however, that the imports of crudes in 1919 are not large enough to account for the exports of nearly 18,000,000 lbs. of dyes, including indigo; so, in the hope of shedding more light on the subject, suppose we lump together the imports of such crudes for 1916, 1917, 1918, and 1919. The total for these years is 49,000,000 lbs., of which Austria supplied 47 per cent and Germany 19 per cent, the rest coming from England, France, and the United States. The largest imports are recorded for 1916, when Austria supplied the bulk of the purchases. For the first six months of 1920, the imports of such crudes were 6,808,000 lbs., or at the rate of about 14,000,000 lbs. for the year, exceeding the average for the four years previous. During these six months, Germany supplied 2.7 per cent and Austria 4.2 per cent, the chief sources of supply being England, the United States, and France. It will be observed that Germany and Austria supplied a considerable proportion of the crudes imported over a period of four and a half years, but that this proportion is gradually being reduced.

Another point is to be considered. Are German-finished dyes imported into Switzerland for reexport? According to the statistics, only to a slight extent. In 1919, a total of 516,000 lbs. came from Germany for consumption in Switzerland and 25,000 lbs. for reexport. For the first six months of 1920 the imports for consumption amounted to 649,000 lbs., practically all of which originated in Germany, with small amounts from Austria and Czechoslovakia. Dyes imported for reexport during the same period are not shown.

In view of the foregoing facts, can it be assumed that

dyes are coming into this country from Switzerland that ought to be excluded? The writer hesitates to express an opinion. There may be, but it is practically impossible to prove it. If an importer is told that the dyes he is importing are not made of materials of German or Austrian origin and he makes affidavit to that effect, how is it possible to prove that he is in error? If identical dyes can be made from German and English crudes and both materials are used in the same Swiss plant, is it possible to identify the dyes made from the German material? And if it is possible, can the limited staff of the present War Trade Board conduct the necessary investigations?

Turning again to the status of the Swiss dye industry, it is interesting to note that the three big concerns have pooled their interests for a period of fifty years and can be assumed to be operating and marketing their product on an efficient basis. They seem confident of the future and are counting on a continuance of their profitable new connections in such quarters as Alsace-Lorraine and Belgium. They recognize certain serious handicaps, chiefly the exchange rate. Swiss money is at a high premium in most European countries, whereas German money is very cheap. Also, Swiss workmen have recently gained the eight-hour day and higher pay, a fact that is cited over and over by all Swiss writers on financial and business topics. Nevertheless, the pessimism concerning other branches of the chemical industry is almost entirely missing in current discussions of the future of the dye industry.

ELECTROCHEMICAL INDUSTRIES

The war greatly stimulated the development of hydroelectric power in Switzerland, as there was a serious shortage of coal from the beginning of hostilities. The available waterpower is estimated at 4,000,000 horsepower, of which 500,000 horsepower had been utilized by 1914. At the end of 1919 new installations had raised the total to 720,000 horsepower, an increase of nearly 50 per cent.

The carbide plants were especially active during the war, for it was never possible to meet the demands from the belligerent countries. From a production of 7500 tons in 1913 there was a continual increase until a total of 40,000 tons was reached in 1918. Then came the post-war slump and production fell off to 10,000 tons, with no signs of immediate recovery. The capacity for manufacturing carbide in Europe now exceeds the peace-time demand and the Swiss are not hopeful of the future. As in other countries, attention has been directed to the increased manufacture of cyanamide from carbide, using the air-nitrogen facilities developed during the war, but the Swiss peasant is rather skeptical about the value of this fertilizer and has welcomed the return of other artificial manures with which he was well acquainted before the war. Owing to the small size of the country, most of the plants that make carbide are within easy reach of communities that are turning to electricity for lighting and heating as the result of the long-continued coal shortage, and these plants are making the best of the opportunity to sell current for such purposes. They will make carbide as a side line in the future.

¹ Under this heading in the Swiss statistics are included benzene, toluene, xylene, anthracene, naphthalene, anthracene oil, chloride of naphthalene, nitronaphthalene, dinitrotoluene, benzoic acid, carbolic acid, etc.

Nevertheless, it is reported that seven of the fifteen plants in operation in 1918 were closed in 1919.

The aluminium plants were also stimulated by the war. They manufacture a high-grade metal and first-class wares, and have been able to continue operations during the post-war period. Employment was steady in 1919, when the carbide industry was so hard hit, but business was naturally not so good as during the war. The exchange rate is the principal handicap.

Plants that manufactured nitric acid during the war are turning their attention to sodium nitrate and calcium nitrate, but the farmers are not enthusiastic users of the latter. The electrolytic production of caustic soda, bleaching powder, and chlorine is of some importance and was reported active in 1919.

The manufacture of ferroalloys, especially ferrosilicon and ferrochrome, is a promising industry, although it has experienced a post-war slump almost as serious as that affecting the carbide industry. The output of ferrosilicon has been as high as 16,000 tons a year. The production of abrasives in connection with the electrochemical industry is also noteworthy.

DRUGS AND PHARMACEUTICALS

Although no longer ranking with the dye industry in importance, the manufacture of drugs is still flourishing in Switzerland. The period of greatest prosperity was during the war and the influenza epidemic, but business has been fairly good since then. Competition from English and American manufacturers is felt on the Continent in some lines, and considerable anxiety is felt on the score of the return of German products. A full line of vegetable alkaloids is produced, the exports amounting to over 51,000 lbs. in 1919 as compared with 44,000 lbs. in 1913, the increase in value, of course, being much greater. The manufacture of synthetic drugs has been developed along with the dye industry, and the products are considered to be of fine quality. The statistics do not give details as to the varieties of drugs exported.

PERFUMERY AND COSMETICS

The manufacture of artificial scents came into prominence in Switzerland between 1890 and 1900, and has grown into an important industry since. It goes hand in hand with the dye and medicinal industries. There is also a considerable output of natural scents. The exports of finished perfumes and cosmetics amounted to over \$1,200,000 in 1913. The total for 1919 was somewhat below that of 1913 in quantity, but prices were up during the period of luxury-buying that followed the armistice. It is an industry that suffers during periods of business depression such as marked the latter half of 1920.

As compared with 1913, the export trade in soaps, both toilet and common, showed a big increase in 1919, although at best it is not comparatively a large trade. The Swiss manufacturers were caught with large stocks of high-priced oils on their hands when the slump in prices came.

HEAVY CHEMICALS

Switzerland is naturally not a large producer of heavy chemicals, as there are few domestic raw ma-

terials and the geographical position of the country makes the cost of importing such materials prohibitive. The only soda factory was compelled to suspend operations for a time during the war, but was later operated as an essential war-time institution in spite of the high price of coal. In 1914 there was only one sulfuric acid plant, but the great chemical plants at Basle later established a plant for the manufacture of sulfuric and hydrochloric acids. Domestic supplies of nitric acid are more than adequate as a result of the development of nitrogen fixation plants during the war. Heavy chemicals are manufactured to some extent by electrolytic processes, as mentioned elsewhere.

THE MARKET FOR IMPORTS

Bearing in mind the size of the country, it will be seen in the following table that Switzerland imports chemicals on a fairly large scale—that is, heavy chemicals. The source of supply has been European rather than American, however. In normal times dependence is placed pretty largely upon Germany and to a lesser extent upon England. American participation has been irregular and incidental and confined to a comparatively few articles—a few acids, denatured alcohol, tin salts, dyeing extracts, phosphate, turpentine, and pharmaceuticals. A table showing the import trade in detail follows:

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS			
CHEMICALS:	1913 Pounds	1916 Pounds	1919 Pounds
Acetate of:			
Aluminum.....	2,650	3,530
Chromium, pyrolignite of iron	194,450	33,730	16,530
Lead, nitrate of lead.....	34,170	1,980	146,390
Germany.....	33,510	440	48,280
United Kingdom.....	1,540	98,110
Acetylene, liquefied under pressure.....	6,830	33,950	440
Acids:			
Acetic and lactic; methanol, crude; acetone; methyl-ethylacetone; preparations with pyridine base..	4,449,810	4,534,020	2,079,400
Austria-Hungary.....	334,250	610,460	182,540
France.....	19,400	66,800	177,910
Germany.....	1,696,020	552,260	1,026,910
United Kingdom.....	10,140	949,530	291,010
United States.....	695,560	2,262,600	253,750
Arsenic; antimony compounds, n. e. s.; chloride of sulfur; bisulfide of calcium; sulfide of arsenic.....	99,430	17,420	15,430
Germany.....	79,810	15,650	15,210
Arsenious (white arsenic); chlorides of barium, calcium, and manganese; magnesium carbonate and sulfate.....	2,169,560	4,466,120	1,146,840
Austria-Hungary.....	220	119,710	111,770
Germany.....	1,408,310	4,078,990	1,024,710
United States.....	2,200	11,680	2,200
Boric and phosphoric.....	69,670	231,050	244,710
France.....	11,240	146,390	11,240
Germany.....	57,540	440	6,390
Italy.....	220	61,950	106,700
United States.....	29,100
Citric and tartaric.....	351,200	378,310	122,360
France.....	78,930	106,700	50,270
Germany.....	162,920	3,310
Italy.....	106,260	250,450	68,560
Hydrochloric.....	17,302,090	1,569,030	2,533,110
Austria-Hungary.....	277,780	549,610
France.....	1,302,270	899,700	283,520
Germany.....	15,987,050	7,500	1,650,380
Nitric.....	503,090	648,820	615,090
France.....	41,230	494,940	14,110
Germany.....	425,270	660	587,970
Oxalic, oxalate of potassium.....	119,930	545,640	366,630
Germany.....	119,930	545,640	303,360
Sulfuric, sulfurous acid in aqueous solution.....	21,189,510	2,677,070	5,019,480
Austria-Hungary.....	709,230
France.....	1,515,900	1,289,040	1,936,320
Germany.....	19,531,890	20,720	1,957,480
Italy.....	48,720	1,011,040	354,500
Sulfuric, fuming; chlorosulfuric acid.....	3,873,300	1,430,580	2,323,450
Austria-Hungary.....	676,600
France.....	272,490	560,190	1,242,960
Germany.....	3,597,060	16,750
United Kingdom.....	440	870,390	115,960

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (Continued)				IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (Continued)			
CHEMICALS (Continued):	1913	1916	1919	CHEMICALS (Continued):	1913	1916	1919
Acids (Concluded):	Pounds	Pounds	Pounds	Potassium (Concluded):	Pounds	Pounds	Pounds
Tannic, gallic, gallaminic....	70,550	112,440	7,280	Pyrolygnite and phenate; barium nitrate; lead sulfide; iron sulfide; zinc powder.	3,343,310	2,913,190	1,091,950
Acids, liquid, n. e. s.....	16,090	9,700	12,790	France.....	1,348,130	276,900	280,870
Alcohol:				Germany.....	1,395,740	1,668,020	340,390
Amyl (fusel oil).....	32,190	12,790	82,230	United Kingdom.....	5,510	365,970	301,590
Denatured spirits of wine....	15,584,920	9,648,530	6,560,730	United States.....	225,970	525,800	1,100
Austria-Hungary.....	6,870,700	16,530	Sodium:			
Russia.....	8,310,900	830,700	Acetate, hyposulfite, fluosilicate.....	755,080	916,020	471,130
Dutch East Indies.....	306,440	3,028,270	Belgium.....	252,210	22,050
United States.....	7,727,420	1,958,140	France.....	108,020	343,480	233,910
Methanol, pure; collodion; organic compounds of bromine, chlorine, iodine; phosgene; other similar products.....	3,018,790	2,956,620	2,680,600	Germany.....	394,850	167,330	136,470
Germany.....	2,664,730	328,050	348,990	United States.....	205,030
Spain.....	929,030	Arsenate, bicarbonate, sulfite, and bisulfite.....	1,587,770	990,100	1,405,220
United Kingdom.....	48,060	1,519,640	392,640	France.....	41,890	211,200	264,110
United States.....	101,190	491,850	664,250	Germany.....	1,532,430	590,840	756,400
Aluminium sulfate; hydrate of alumina; sodium aluminate; chloride, sesquichlorate, and fluoride of chromium; thiocyanate of aluminium.....	8,803,060	59,220,790	32,250,320	United Kingdom.....	5,070	27,560	179,020
Germany.....	8,325,540	57,526,090	32,046,390	Borate (borax).....	707,680	1,198,430	604,290
United States.....	788,370	France.....	97,440	700,850	18,960
Alums.....	245,370	3,526,510	238,320	Germany.....	597,670	220
Germany.....	211,200	3,107,630	200,840	United Kingdom.....	3,970	269,620	466,500
Ammonia:				United States.....	108,910
In aqueous solution.....	186,070	440	1,388,030	Carbonate:			
Germany.....	181,440	440	1,299,620	Crystals.....	769,190	30,640	3,300
Liquefied under pressure.....	17,640	1,320	Soda ash.....	34,413,270	19,340,710	224,210
Ammonium muriate (sal ammoniac).....	400,800	169,320	411,600	France.....	1,344,160	223,990
Germany.....	396,390	168,880	311,950	Germany.....	33,965,290	14,820,350	220
Bromine and iodine and salts.....	131,840	111,990	286,820	United Kingdom.....	395,950	803,810
Germany.....	125,000	27,120	247,140	Chromate (bichromate), cyanide, sulfate, sulfide.....	8,934,890	2,921,560	3,560,460
United States.....	49,820	Austria-Hungary.....	377,210	242,950
Calcium:				France.....	2,158,100	245,370	483,250
Carbide.....	68,780	23,590	8,820	Germany.....	6,631,720	1,161,620	2,113,130
Chloride.....	2,648,850	1,320	1,322,990	United Kingdom.....	135,140	904,560	514,560
France.....	258,880	111,110	United States.....	232,810	125,880
Germany.....	2,358,510	1,320	1,150,150	Nitrite.....	998,690	530,870	796,090
Carbon sulfide.....	804,470	787,930	890,670	Phosphate.....	2,079,620	157,630	343,920
Carbonic acid, liquefied.....	352,520	440	440	France.....	71,430	120,370	880
Chlorates, perchlorates, persulfates, n. e. s.....	153,220	220	61,070	Germany.....	2,008,190	4,190	660
Chlorine, liquefied under pressure.....	566,150	440	297,620	United Kingdom.....	33,070	213,190
Chloroform, chloral.....	24,470	14,770	13,230	United States.....	129,190
Copper sulfate and preparations.....	4,636,540	3,908,130	2,341,750	Salts, n. e. s.....	453,710	415,350	309,970
France.....	2,416,040	307,540	46,300	France.....	151,900	31,090	220
United Kingdom.....	689,600	2,392,010	1,482,600	Germany.....	293,880	201,720	136,470
United States.....	222,230	414,030	10,800	Italy.....	6,830	132,940
Ether:				United States.....	93,260	22,050
Acetic.....	10,360	440	Tartar:			
Sulfuric.....	63,490	440	12,350	Crude.....	10,360	440	6,170
Formaldehyde, aldehyde, denatured.....	825,630	701,290	434,750	Cream of; neutral tartrate; tartar emetic.....	63,930	60,410	10,800
Germany.....	824,310	140,430	164,460	Tin salts.....	1,849,240	1,203,500	582,020
United States.....	355,600	196,870	Germany.....	1,598,570	905,780	184,090
Gases, liquefied, n. e. s.....	341,050	41,000	121,920	United States.....	132,060	390,000
Glycerol, glycerol lye.....	604,290	57,320	65,040	Zinc chloride, mother-lye of zinc chloride.....	199,740	88,630	164,690
Hydrogen peroxide.....	313,280	498,460	266,540	Germany.....	192,240	56,880	131,400
Hypochlorites.....	278,220	89,700	93,700	COAL-TAR PRODUCTS:			
Inorganic prepared auxiliary materials, n. e. s.....	1,123,920	767,430	898,380	Coal-tar dyes:			
France.....	143,300	108,470	112,880	Alizarin:			
Germany.....	760,370	547,410	678,140	Germany.....	508,600	134,920	197,530
United States.....	11,900	6,610	34,170	Aniline, anthracene, naphthalene dyes; coal-tar dyes, n. e. s.....	1,539,270	949,750	489,200
Iodoform.....	2,650	220	1,100	Germany.....	1,476,660	949,750	475,090
Iron sulfate, zinc sulfate.....	1,118,850	194,230	89,510	Indigo, natural or synthetic.....	153,440	17,200	41,230
Lactarin (casein), extract of rennet.....	399,920	332,240	363,540	Germany.....	152,560	17,200	41,230
France.....	306,440	239,640	242,510	Other products:			
United States.....	48,060	Aniline, aniline oil.....	2,649,510	2,848,810	815,710
Lead oxide.....	210,710	110,010	52,250	France.....	47,400	56,220
Magnesium chloride.....	6,527,890	4,412,330	4,366,690	Germany.....	2,591,970	13,670
Germany.....	6,432,200	4,412,330	4,263,520	United Kingdom.....	57,540	2,314,630	745,820
Milk sugar, whey powder.....	26,680	51,150	16,310	United States.....	486,780
Peroxides of barium, lead, sodium.....	749,130	895,080	591,500	Aniline compounds for the manufacture of dyes.....	1,956,160	280,210	939,830
Germany.....	609,580	719,810	588,190	France.....	6,170	32,850	17,190
Phosphorus:				Germany.....	1,871,280	4,410	142,420
Red (amorphous).....	83,780	28,220	54,010	United Kingdom.....	78,710	199,960	727,090
White.....	107,810	24,470	38,360	United States.....	42,990	53,130
Potash, crude.....	848,340	1,749,590	194,230	Benzyl chloride, nitrobenzene, naphthol and its derivatives.....	2,388,050	841,280	1,697,340
Potassium:				France.....	325,180	488,770
Hydroxides of potassium and sodium, solid.....	19,635,250	18,715,260	6,382,820	Germany.....	2,377,020	4,410	240,960
Austria-Hungary.....	1,849,900	506,400	United Kingdom.....	470,020	803,140
France.....	1,026,030	3,397,760	3,040,830	United States.....	9,920	41,670	152,340
Germany.....	18,595,770	9,291,820	290,790	Coal-tar derivatives for the manufacture of dyes (benzene, toluene, etc.).....	7,331,690	25,038,330	5,290,870
United Kingdom.....	220	3,114,690	2,469,400	Austria-Hungary.....	660	16,645,560	720,030
United States.....	1,060,860	44,310	France.....	401,020	927,920	1,494,290
Hydroxides of potassium and sodium, liquid (lye).....	1,501,120	1,402,800	259,040	Germany.....	6,232,250	4,708,850	1,428,180
Nitrate, and nitrate of sodium (pure).....	1,653,910	1,179,250	214,070	United Kingdom.....	689,600	2,433,460	1,509,730
Germany.....	834,230	13,230	138,670	United States.....	228,460	89,730
United Kingdom.....	1,760	579,160	Phthalic acid, resorcinol.....	207,010	32,850	107,360
United States.....	104,060	3,970	Saccharin.....	3,750	880	11,020
Prussiate, bichromate, permanganate, thiocyanate, cyanide.....	987,670	228,180	974,000	Salicylic acid.....	139,330	116,840	168,210
Austria-Hungary.....	149,470	71,430	805,130	Tar-oil derivatives (carbolineum, creosote, creosote oil, creolin, lysol, etc.).....	7,086,220	2,127,460	23,563,450
Germany.....	769,190	151,240	136,020	France.....	14,770	267,860	1,593,720
United States.....	14,770	Germany.....	6,906,420	827,610	21,752,350
Silicate, and silicate of sodium (water glass).....	5,648,020	4,450,470	3,411,430	United Kingdom.....	14,330	996,710	95,900
France.....	314,820	1,215,190	United States.....	47,180
Germany.....	5,308,290	3,211,030	3,411,430	DYEING AND TANNING MATERIALS:			
				Extracts for dyeing.....	1,165,140	854,730	1,111,790
				France.....	201,280	93,260	65,480
				Central America.....	299,170	19,840	342,380
				United States.....	465,840	531,750	668,080

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (Continued)

	1913 Pounds	1916 Pounds	1919 Pounds
DYEING, ETC. (Concluded):			
Extracts for tanning.....	5,793,530	5,592,900	7,658,860
France.....	3,644,460	19,840	373,240
Italy.....	1,281,330	1,158,530	263,230
Argentina.....	374,340	2,209,690	6,999,670
United States.....	28,220	1,776,270	3,970
EXPLOSIVES:			
Guncotton, pyroxylin.....	35,720	4,630	4,630
Dynamite and other explosives, n. e. s.....	221,340	166,230	9,260
Fireworks and pyrotechnical preparations.....	22,930	10,360	29,100
FERTILIZERS:	Metric Tons	Metric Tons	Metric Tons
Chile saltpeter, ammonium sul- fate.....	3,328	343	1,078
Phosphates, crude; bone meal, etc.....	18,885	7,457	14,859
Belgium.....	2,083	5,410	329
France.....	1,565	4,832	4,832
Germany.....	2,114	3	21
Algeria-Tunis.....	3,045	2,004	7,145
United States.....	8,882	2,530	2,530
Potash fertilizers, Stassfurt salts	13,241	22,808	29,336
France.....	18	15,361	15,361
Germany.....	13,223	22,808	13,945
Potassium muriate.....	1,572	82	4,776
France.....	1,572	10	4,685
Germany.....	1,572	72	41
Slag, basic.....	55,793	29,922	46,443
France.....	7,992	1,985	32,826
Germany.....	47,749	27,937	9,337
Sulfuric acid, used.....	1,994	257	110
Superphosphates and other pre- pared fertilizers.....	26,309	1,776	3,215
France.....	4,833	1,761	37
Germany.....	15,537	5	16
Algeria-Tunis.....	3,030
United States.....	102
MEDICINAL PREPARATIONS AND DRUGS:	Pounds	Pounds	Pounds
Alkaloids, vegetable.....	24,910	6,390	46,740
Germany.....	11,900	3,310	34,390
Balsams, concentrated juices of plants, medicinal oils.....	695,780	500,450	366,400
Chemical products, n. e. s., for pharmaceutical use.....	702,170	274,700	260,800
Foods, artificial (somaose, etc.)	35,940	7,050	8,380
Pharmaceutical products, n. e. s. (pills, powders, plasters, tinctures, etc.).....	1,031,980	534,620	646,390
France.....	308,210	329,810	341,060
Germany.....	522,270	78,040	152,340
Italy.....	95,240	78,930	76,060
United States.....	22,710	1,320	30,860
Sera, vaccines.....	4,630	2,650	5,290
Spring salts and marsh salts.....	32,630	48,060	19,620
OILS, VEGETABLE:			
Fixed or expressed:			
Castor:			
Crude.....	679,020	115,300	358,250
Colorless, purified.....	105,600	16,530	65,040
Coconut, palm, and other.....	4,829,670	6,142,960	6,515,980
France.....	1,213,200	3,315,090	175,930
Germany.....	2,315,730
Italy.....	278,000	1,366,650	360,900
Dutch East Indies.....	22,050	1,224,890
Japan.....	2,229,970	577,830
Africa.....	646,830	381,840	296,520
United States.....	5,381,260
Linseed.....	10,514,060	5,542,640	267,200
Belgium.....	5,338,930	660
France.....	1,593,940	3,554,290	992,520
Netherlands.....	2,972,930	1,558,230	324,080
Spain.....	257,940	746,040
Dutch East Indies.....	1,395,970
Japan.....	49,380
United States.....	11,460
Olive:			
Denatured.....	1,381,860	2,675,310	2,872,400
France.....	591,600	1,816,830	160,060
Spain.....	835,330	2,625,040
United States.....	48,720	48,280
Edible.....	1,875,030	1,947,560	5,256,700
France.....	927,930	697,980	272,490
Italy.....	682,110	630,080	271,830
Spain.....	156,310	499,790	4,711,940
United States.....	20,280	440
Peanut, rape, hemp, sesame, cottonseed, and other, for industrial purposes.....	6,321,090	7,757,400	4,731,340
Belgium.....	1,034,850	50,270
France.....	1,977,990	2,463,000	39,900
Italy.....	2,200	326,720
United Kingdom.....	1,635,610	292,770	221,790
Dutch East Indies.....	628,760
Japan.....	251,550	2,115,130	2,883,200
United States.....	678,800	709,000	259,270
Turkey-red oil and other sulfo- ricinoleates.....	335,540	232,810	25,130
Oils, edible, n. e. s.....	20,764,680	19,015,750	19,760,470
Belgium.....	2,412,520
France.....	10,471,510	13,132,930	555,780
Spain.....	1,457,480
United States.....	5,366,930	5,528,750	15,472,480
Germany.....	1,979,970	220
Volatile or essential:			
For pharmaceutical use and perfumery (rose, violet, cajeput, nutmeg, pine- needle, bitter-almond, eucalyptus).....	26,460	58,860	29,540

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (Continued)

	1913 Pounds	1916 Pounds	1919 Pounds
OILS, VEGETABLE (Concluded):			
Volatile or essential (Concluded):			
France.....	9,260	17,640	17,860
Germany.....	13,890	18,960	6,390
Other (cloves, lavender, aspic, juniper; ethers with fruit odor).....	272,930	476,420	539,250
France.....	32,410	39,240	106,480
British India.....	102,960	86,860	80,690
United States.....	2,650	4,850	55,560
PAINTS, PIGMENTS, VARNISHES:			
Chemical colors, dry, not pre- pared:			
Black, lampblack, bone black.....	509,040	2,704,190	328,270
Germany.....	455,700	2,607,630	242,950
United States.....	15,430	10,360	37,920
Cinnabar, Prussian blue, ul- tramarine, Schweinfurt green, bronze colors.....	289,250	276,680	261,910
France.....	44,310	37,700	61,290
Germany.....	219,360	235,670	165,790
United States.....	220	3,310
Color varnishes (carmine, ge- ranium, scarlet, viridin)....	173,060	475,540	142,640
Lead:			
Red.....	539,910	67,680	122,140
White.....	845,690	108,470	181,000
Yellow.....	440
Lithopone, pearl white.....	2,069,920	2,504,890	659,400
Germany.....	1,743,420	2,252,680	569,230
Victoria green.....	140,430	80,910	33,730
Zinc white, zincolithe.....	1,779,350	1,808,670	866,200
Belgium.....	403,000	11,020
Germany.....	776,690	1,555,140	659,400
Other (chrome yellow and green; mineral blue; smalt; zinc green, etc.).....	450,400	275,800	194,670
Colors of all kinds, prepared:			
Chrome oxide and other colors, n. e. s., in water paste.....	184,750	406,750	24,690
Oil varnishes (linseed oil and poppyseed oil, boiled, fluid).....	46,960	81,130	154,100
White casein or glue colors (alabastine, amphiboline, in- durine, etc.).....	117,250	59,080	20,720
White lead.....	917,120	1,980	1,980
Zinc white, pearl white.....	622,360	13,000	34,390
Other prepared colors.....	452,170	302,690	183,200
Germany.....	362,660	258,600	135,140
United States.....	2,200	220	6,830
Varnishes, lacs, and siccatives..	1,722,030	549,610	478,180
France.....	219,360	161,380	117,950
Germany.....	1,088,420	157,190	127,430
United Kingdom.....	168,650	100,970	118,830
United States.....	39,900	55,340	76,280
PERFUMERY AND COSMETICS:			
In containers weighing more than 1 kilo.....	56,880	152,780	64,150
France.....	15,870	33,950	17,640
Germany.....	36,380	109,130	35,710
United States.....	220	1,100	1,100
In containers weighing 1 kilo or less.....	264,780	262,570	373,240
France.....	119,710	160,940	241,400
Germany.....	104,940	81,350	56,660
United States.....	3,530	3,750	23,810
OTHER PRODUCTS:			
Albumin.....	415,350	18,520	10,140
United States.....	335,540
Blackening and polishes:			
In containers weighing 5 kilos or more.....	210,540	70,100	17,200
In containers weighing less than 5 kilos.....	822,320	426,370	221,340
Germany.....	676,600	256,400	103,400
United Kingdom.....	72,750	79,800	39,240
United States.....	7,940	31,750	29,760
Candles:			
Ball tapers, Christmas tree candles, colored or orna- mental candles.....	45,860	660	1,760
All other.....	70,770	20,280	23,150
Dextrin.....	70,770	419,100	142,640
Glue:			
For joiners, house painters, plasterers.....	1,253,330	783,740	328,270
Germany.....	932,330	462,310
France.....	177,030	175,490	149,250
United States.....	2,420	880
Gelatin, fish glue.....	231,050	134,920	39,240
Liquid or in powder.....	178,130	108,690	33,510
Liquid, for office use.....	52,030	37,040	29,320
Ink:			
Printing.....	495,160	442,690	133,600
Writing and other.....	327,380	229,720	214,290
Germany.....	264,770	199,520	187,390
United States.....	4,410	440	660
Paper and pulp:			
Paper:			
Newsprint.....	732,590	121,700	3,935,910
Germany.....	697,540	121,700	633,610
Sweden.....	3,145,770
Other printing, writing, and drawing paper.....	9,630,010	10,405,160	6,747,030
Germany.....	7,557,220	8,043,120	5,283,380
United States.....	13,230	54,670	24,910
Packing.....	5,079,010	4,642,050	8,457,370
Germany.....	3,005,780	2,941,850	5,288,450
Sweden.....	686,740	511,690	1,065,270

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (Concluded)			
OTHER PRODUCTS (Concluded):	1913	1916	1919
Paper and pulp (Concluded):	Metric Tons	Metric Tons	Metric Tons
Paper pulp:			
Chemical.....	10,476	9,461	12,160
Germany.....	6,539	87
Sweden.....	1,867	9,074	9,929
Russia.....	120	1,661
Mechanical.....	1,590	2,198	1,117
Pitch, unmanufactured.....	2,589	1,321	22,219
Germany.....	2,330	989	18,842
	Pounds	Pounds	Pounds
Resins, manufactured (brewers' and shoemakers' pitch, etc.)	768,530	50,040	58,200
Rosin.....	6,209,520	7,785,400	3,190,530
France.....	3,081,180	6,543,540	1,443,370
Spain.....	554,020	1,713,650
United States.....	2,040,110	888,890	29,540
Soap:			
Common, in bulk, cases, casks; in lumps, cakes, etc.; soft soap.....	4,625,300	4,435,920	6,195,870
France.....	4,120,880	2,913,190	1,082,910
Spain.....	88,620	4,756,690
United States.....	9,260	20,060	97,220
Other (toilet, medicinal, special soaps).....	475,310	149,250	313,060
France.....	93,480	91,050	130,290
Germany.....	285,940	9,700	5,290
United States.....	12,570	18,960	46,520
Soap powder and preparations for laundries.....	1,645,750	320,550	46,960
Germany.....	1,521,190	319,670	20,720
Soap waste.....	848,120	43,650	18,740
Starch gum, preparations for sizing and finishing.....	1,483,930	597,890	122,580
	Metric Tons	Metric Tons	Metric Tons
Sugar, raw and refined; glucose, solid.....	117,261	110,358	104,927
Austria-Hungary.....	74,917	11,014	326
France.....	7,600	16	84
Germany.....	33,229	10,917	2,486
Netherlands.....	9	9,067	694
Dutch East Indies.....	4	31,131	88,096
Central America.....	6	3,533
United States.....	14	48,213	1,283
	Pounds	Pounds	Pounds
Tar.....	2,447,350	173,060	2,998,730
Turpentine, white resin.....	188,270	66,800	6,390
Spirits of.....	4,259,990	3,274,970	3,405,040
France.....	1,835,570	1,953,740	641,330
Spain.....	2,371,730	887,580	2,491,440
United States.....	35,270	433,650	272,270

THE EXPORT TRADE

The following table shows in detail the exports of chemicals and allied products according to official figures for 1913, 1916, and 1919. In the absence of any recent census of manufactures these figures will be a guide in estimating production, as a very large proportion of most manufactured chemicals are exported.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS			
CHEMICALS:	1913	1916	1919
	Pounds	Pounds	Pounds
Acetate of:			
Chromium, pyrolignite of iron	128,970	392,640	5,510
Lead, nitrate of lead.....	10,360	2,200	5,290
Acetylene, liquefied under pressure.....	12,120	2,870
Acids:			
Acetic and lactic; methanol, crude; acetone; methyl-ethylacetone; preparations with pyridine base.....	1,067,040	137,350	91,270
Germany.....	574,080
Italy.....	186,510	94,800	76,060
Arsenic; antimony compounds, n. e. s.; chloride of sulfur; bisulfide of calcium; sulfide of arsenic.....	1,320	440
Arsenious (white arsenic); chlorides of barium, calcium, and manganese; magnesium carbonate and sulfate.....	40,560	423,950	274,470
France.....	5,070	416,450	34,610
Italy.....	31,300	239,200
Boric and phosphoric.....	217,600	81,570	29,320
Citric and tartaric.....	6,170	440	13,670
Hydrochloric.....	1,568,590	45,860	201,500
Nitric.....	1,178,150	24,250	837,100
Germany.....	1,173,740	24,250	11,020
Italy.....	697,760
Oxalic, oxalate of potassium..	160,720	64,370	8,600
Sulfuric, sulfurous acid in aqueous solution.....	2,604,980	18,300	185,410
Germany.....	2,099,680	31,750
Sulfuric, fuming; chlorosulfuric acid.....	440
Tannic, gallic, gallaminic.....	520,950	344,360	281,750
France.....	35,720	185,190	156,090
Germany.....	294,320	7,500
United Kingdom.....	46,740	67,460	52,030
Acids, liquid, n. e. s.....	22,930	6,610	9,260

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (Continued)			
CHEMICALS (Continued):	1913	1916	1919
	Pounds	Pounds	Pounds
Alcohol:			
Amyl (fusel oil).....	3,750
Denatured spirits of wine.....	2,200	1,980	1,760
Methanol, pure; collodion; organic compounds of bromine, chlorine, iodine; phosgene; other similar products.....	147,050	362,000	182,320
France.....	95,680	68,120	111,110
United Kingdom.....	1,760	237,660	27,780
Aluminium sulfate; hydrate of alumina; sodium aluminate; chloride, sesquichlorate, and fluoride of chromium; thiocyanate of aluminium.....	14,550	1,320
Alums.....	2,420	152,560	25,350
Ammonia:			
In aqueous solution.....	215,610	164,020	103,180
Liquefied under pressure.....	2,650	31,530	8,820
Ammonium muriate (sal ammoniac).....	4,850	880	39,240
Bromine and iodine and their salts.....	1,540	660	11,680
Calcium:			
Carbide.....	70,085,830	127,889,700	81,332,040
Belgium.....	5,180,200	1,522,070	88,180
France.....	78,700	22,840,990	26,690,260
Germany.....	55,144,660	101,990,020	53,868,850
Netherlands.....	5,888,550	44,090	44,090
Portugal.....	3,593,530
Rumania.....	462,970	347,450
Chloride.....	300,490	1,336,000	724,000
France.....	1,980	1,203,280	489,870
Italy.....	63,710	130,070	233,470
Austria-Hungary.....	228,620	2,650
Carbonic acid, liquefied.....	8,820	146,170	330,690
France.....	8,820	124,340	328,050
Chlorates, perchlorates, persulfates.....	4,911,910	2,462,120	1,215,850
Belgium.....	451,730	216,710
France.....	316,580	34,170	11,680
Germany.....	678,360	79,150	74,960
Japan.....	1,444,910	932,340	223,990
Australia.....	427,700	33,730
Chlorine, liquefied under pressure.....	431,890
Chloroform, chloral.....	22,050	24,910	40,790
Copper sulfate and preparations	136,240	5,730	3,530
Ether:			
Acetic.....	440	220
Sulfuric.....	14,110	3,300	6,610
Formaldehyde, aldehyde, denatured.....	220	2,650	160,500
Gases, liquefied, n. e. s.....	56,220	9,260	1,980
Glycerol, glycerol lye.....	1,160,950	671,300	139,990
France.....	76,280	92,150
Germany.....	366,190
United States.....	521,390	403,670
Hydrogen peroxide.....	16,760	51,590	356,040
Hypochlorites.....	81,570	60,190	75,400
Inorganic prepared auxiliary materials, n. e. s.....	1,584,240	2,459,480	201,940
Austria-Hungary.....	10,140	466,280	132,940
France.....	19,840	1,112,230	26,450
Germany.....	1,458,580	627,210	4,630
United States.....	440	5,070	3,530
Iodoform.....	5,070	5,510	1,540
Iron sulfate, zinc sulfate.....	675,940	590,400	9,700
Lactarine (casein), extract of rennet.....	7,940	303,360	41,670
Germany.....	3,750	303,140	33,070
Lead oxide.....	16,980	2,200	440
Magnesium chloride.....	232,590	84,220	49,160
Milk sugar, whey powder.....	1,100	21,160	440
Peroxides of barium, lead, sodium	8,160	5,510
Potash, crude.....	1,540	52,470	30,200
Potassium:			
Hydroxides of potassium and sodium:			
Solid.....	10,580	24,250	5,290
Liquid (lye).....	15,430	30,200
Nitrate, and nitrate of sodium (pure).....	14,110	92,370
Prussiate, bichromate, permanganate, thiocyanate, cyanide.....	1,540	19,400	148,810
Silicate and silicate of sodium	22,490	506,840	194,230
Pyrolignite and phenate; barium nitrate; lead sulfide; iron sulfides; zinc powder.....	1,169,770	770,960	502,210
France.....	494,710	149,470	49,600
Germany.....	599,430	212,300	48,720
Italy.....	12,120	366,410	351,200
Sodium:			
Acetate, hyposulfite, fluosilicate.....	22,930	440
Arsenate, bicarbonate, sulfite, and bisulfite.....	249,340	27,560	37,480
Borate (borax).....	2,200
Carbonate:			
Crystals.....	526,020	69,000	28,000
Soda ash.....	1,881,420
Germany.....	244,050
Italy.....	1,412,500
Netherlands.....	223,990
Chromate (bichromate), cyanide, sulfate, sulfide.....	2,732,850	5,061,590	3,865,580
Germany.....	1,030,000	176,150
Italy.....	1,510,390	4,850,610	3,690,540

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (Continued)

CHEMICALS (Concluded):	1913 Pounds	1916 Pounds	1919 Pounds
Sodium (Concluded):			
Nitrite.....	583,780	316,800	162,700
Germany.....	467,820	316,800	10,800
Italy.....	50,930		136,690
Phosphate.....	1,124,360	22,930	961,220
Germany.....	728,410	22,930	193,120
Italy.....	395,730		746,260
Salts, n. e. s.....	1,026,910	908,960	595,470
France.....	54,450	122,580	80,250
Germany.....	317,240	11,020	111,550
Russia.....	144,840	13,450	
Spain.....	20,500	60,850	185,630
United Kingdom.....	54,450	284,400	55,340
Japan.....	122,360	11,020	1,100
United States.....	9,700	281,310	6,610
Tartar:			
Crude.....	290,570	457,460	104,940
Germany.....	50,490	422,180	104,720
United States.....		13,000	
Cream of; neutral tartrate; tartar emetic.....	660	1,100	65,920
Tin salts.....	51,810		
Zinc chloride, mother-lye of zinc chloride.....	22,490	235,670	4,630
COAL-TAR PRODUCTS:			
Coal-tar dyes:			
Aniline, anthracene, naphthalene dyes; coal-tar dyes, n. e. s.....	15,508,860	9,120,520	14,137,230
Austria-Hungary.....	711,650	1,100	18,520
Belgium.....	704,340		838,420
France.....	309,970	632,290	2,516,580
Germany.....	3,586,260	3,750	2,650
Italy.....	1,386,040	1,162,720	1,731,070
Netherlands.....	169,980	55,780	111,110
Norway.....	38,800	21,380	18,300
Russia.....	313,720	68,120	85,320
Spain.....	175,050	272,490	348,330
Sweden.....	158,050	38,580	201,940
United Kingdom.....	1,879,220	4,621,990	5,150,000
British India.....	1,090,180	51,810	492,730
China.....	589,070	84,440	182,540
Japan.....	767,870	132,380	264,990
Brazil.....	91,930	211,420	177,470
Canada.....	144,400	45,190	65,040
United States.....	2,815,300	1,507,520	1,468,720
Indigo, natural or synthetic.....	3,950,240	1,633,850	3,632,340
Belgium.....	235,890		100,090
France.....	1,100	30,420	323,660
Italy.....	80,250	51,370	242,070
Russia.....	55,560	15,430	
United Kingdom.....		607,820	248,680
China.....	2,845,730	245,810	1,893,990
Japan.....	143,960		145,500
United States.....	476,860	605,170	448,420
Other products:			
Aniline, aniline oil.....	11,680		220
Aniline compounds for the manufacture of dyes.....	294,980	76,720	128,310
France.....	95,680	69,220	105,160
Germany.....	136,020		8,820
United States.....	2,200	3,090	
Benzyl chloride, nitrobenzene, naphthol and its deriva- tives.....	178,570	250,450	151,460
France.....	43,650	162,480	135,360
Coal-tar derivatives for the manufacture of dyes (ben- zene, toluene, etc.).....	232,150	606,050	63,490
France.....	2,870	579,600	3,530
Germany.....	218,480		8,900
Phthalic acid, resorcinol.....	1,100		3,750
Saccharin.....	174,160	34,830	168,650
Austria-Hungary.....	1,980	440	115,740
Netherlands.....	47,620	1,100	220
United Kingdom.....	42,330	19,620	
British India.....	31,970	5,510	9,260
United States.....		1,320	7,280
Salicylic acid.....	1,320		
Tar-oil derivatives (carbolium, oil, creosote, creosote oil, etc.).....	23,810	12,570	9,700
DYEING AND TANNING MATERIALS:			
Extracts for dyeing.....	987,230	345,020	271,610
Germany.....	370,160	1,760	16,750
United Kingdom.....	45,420	100,970	55,120
United States.....	56,440	18,740	5,290
Extracts for tanning.....	2,902,600	445,990	1,696,010
France.....	612,440	186,070	181,440
Germany.....	838,860		437,180
Italy.....	26,240	6,170	352,520
Rumania.....			485,020
United States.....	924,400	172,400	1,100
EXPLOSIVES:			
Dynamite and other explosives, n. e. s.....	522,490		1,760
Germany.....	522,270		1,760
Fireworks and pyrotechnic pre- parations.....	5,730	222,000	1,100
Russia.....		210,760	
FERTILIZERS:	Metric Tons	Metric Tons	Metric Tons
Chile saltpeter, ammonium sul- fate.....	29	20	1
Phosphates, crude; bone meal, etc.....	1,500	1,484	20
France.....	966		20
Germany.....	280	1,473	

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (Continued)

FERTILIZERS (Concluded):	1913 Metric Tons	1916 Metric Tons	1919 Metric Tons
Superphosphates and other pre- pared fertilizers.....	10,994	20,619	7,116
France.....	1,238	8,702	5,282
Germany.....	8,623	11,520	1,758
Italy.....	807	396	10
MEDICINAL PREPARATIONS AND DRUGS:	Pounds	Pounds	Pounds
Alkaloids, vegetable.....	44,310	19,620	51,370
France.....	660	880	12,350
Germany.....	37,040	12,350	14,990
Rumania.....		880	1,100
United Kingdom.....	1,100	1,760	1,100
Balsams, concentrated juices of fruits, medicinal oils.....	46,080	11,680	19,180
Chemical products, n. e. s., for pharmaceutical use.....	702,170	493,620	514,780
France.....	90,390	145,280	108,690
Germany.....	161,820	17,200	4,630
Italy.....	40,340	29,980	53,130
Russia.....	106,700	37,480	23,810
Spain.....	9,040	15,870	43,210
United Kingdom.....	39,680	84,660	62,170
Japan.....	53,350	7,500	19,400
United States.....	16,750	88,850	25,130
Foods, artificial (somaose, etc.)	2,713,890	1,980	2,870
Germany.....	2,698,900		220
Pharmaceutical products, n. e. s. (pills, powders, plasters, tinctures, etc.).....	539,470	652,790	703,050
Austria-Hungary.....	51,590	98,550	5,510
Germany.....	209,660	232,150	34,830
Italy.....	16,540	29,540	66,360
Netherlands.....	25,790	35,270	68,120
United Kingdom.....	52,910	48,060	135,140
Argentina.....	18,740	16,310	46,080
United States.....	5,510	24,470	25,130
Sera; vaccines.....	9,700	14,770	14,330
Spring salts and marsh salts.....	660		3,310
OILS, VEGETABLE:			
Fixed or expressed:			
Castor, crude.....			440
Coconut, palm, and other.....	5,730		1,821,240
Austria-Hungary.....			1,490,320
Linseed.....	13,890	1,100	703,930
Olive, denatured.....	20,940		15,870
Peanut, rape, hemp, sesame, cottonseed and other, for industrial purposes.....	3,970	660	36,380
Turkey-red oil and other sulfo- rincolates.....	18,520		2,420
Oils, edible, n. e. s.....	24,470	5,730	316,810
Volatile or essential:			
For pharmaceutical use and per- fumery (rose, violet, etc.)...	27,780	11,900	7,280
Other (cloves, lavender, aspic, juniper; ethers with fruit odor.....	10,362	41,890	25,350
PAINTS, PIGMENTS, COLORS, VAR- NISHES:			
Chemical colors, dry, in lumps or powder, not prepared:			
Black, lampblack, bone black	880	45,860	1,760
Cinnabar, Prussian blue, ultra- marine, Schweinfurt green, bronze colors.....	1,760	30,640	34,390
Color varnishes.....	1,540	307,100	45,640
Lead:			
Red.....	4,190	440	440
White.....	2,200	178,790	94,800
Lithopone, pearl white.....	1,540		880
Zinc white, zinc litho.....	2,650		1,320
Other (chrome yellow and green; mineral blue; smalt; zinc green, etc.).....	1,760	4,190	44,970
Colors of all kinds, prepared:			
Chrome oxide and other colors, n. e. s., in water paste.....	9,920	8,820	220
Oil varnishes (linseed oil and poppyseed oil, boiled, fluid)	27,340	18,520	30,640
White casein or glue colors (alabastine, amphiboline, in- durine, etc.).....	1,760	1,760	1,540
White lead.....	7,050	488,320	939,390
France.....	4,410	488,320	938,730
Zinc white, pearl white.....	5,290	116,180	2,870
Other prepared colors.....	20,500	162,040	69,450
Varnishes, lacs, and siccatives...	153,880	959,450	358,690
Austria-Hungary.....	1,760	64,150	49,820
France.....	71,430	21,600	36,000
Germany.....	46,080	843,710	259,040
PERFUMERY AND COSMETICS:			
In containers weighing more than 1 kilo.....	203,050	315,700	204,150
France.....	20,060	67,900	70,990
Russia.....	15,210	44,310	440
United Kingdom.....	55,120	51,150	30,420
United States.....	48,940	26,240	18,520
In containers weighing 1 kilo or less.....	340,610	151,020	216,710
France.....	20,940	4,400	3,970
Rumania.....	660	32,850	25,790
Russia.....	5,070	880	8,600
United Kingdom.....	6,830	2,650	5,730
Japan.....	7,720	12,570	3,310
Brazil.....	242,070	5,070	77,160
United States.....	7,940	4,190	11,680
OTHER PRODUCTS:			
Albumin.....	13,010	2,420	1,100
United States.....	5,510		880

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (Continued)			
	1913	1916	1919
Pounds	Pounds	Pounds	Pounds
OTHER PRODUCTS (Continued):			
Blacking and polishes:			
In containers weighing 5 kilos or more.....	67,460	429,020	89,730
In containers weighing less than 5 kilos.....	166,010	100,310	116,850
Candles:			
Ball tapers, Christmas tree candles, colored or ornamental candles.....	660	20,500	1,320
All other.....	58,860	209,220	33,950
Dextrin.....	352,080	1,100	11,680
Glue:			
For joiners, house painters, plasterers.....	2,914,950	2,631,000	3,953,770
France.....	263,450	891,770	1,084,670
Germany.....	1,658,540	580,920	2,442,280
Italy.....	921,310	144,620	178,130
United Kingdom.....	19,620	697,320	38,360
United States.....	16,310	139,770	33,070
Gelatin, fish glue.....	432,330	413,140	300,270
France.....	18,300	88,180	57,980
United Kingdom.....	93,480	108,910	91,270
United States.....	160,720	39,020	29,320
Liquid or in powder.....	12,350	105,600	23,590
Liquid, for office use.....	10,140	1,760	9,480
Ink:			
Printing.....	7,060	126,100	15,650
Writing and other.....	31,970	100,090	86,200
Paper and pulp:			
Paper:			
Newsprint.....	23,810	2,474,250	3,771,890
Belgium.....			446,000
France.....	23,590	2,474,030	2,817,510
Italy.....		220	472,450
Other printing, writing, and drawing paper.....	514,780	1,973,140	2,735,050
France.....	64,600	1,347,900	1,599,680

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (Concluded)			
	1913	1916	1919
Pounds	Pounds	Pounds	Pounds
OTHER PRODUCTS (Concluded):			
Paper and Pulp (Concluded):			
Germany.....	123,460	50,040	17,649
Italy.....	130,730	218,920	731,490
United States.....	31,750	174,380	
Packing.....	495,600	2,875,930	2,278,700
France.....	199,740	2,720,060	1,427,270
Italy.....	95,680	20,720	665,580
Paper pulp:	Metric Tons	Metric Tons	Metric Tons
Chemical.....	4,831	4,890	7,092
France.....	3,193	3,715	2,946
Italy.....	1,532	1,175	4,075
Mechanical.....	1,818	1,765	2,238
France.....	1,702	1,700	2,192
Pitch, unmanufactured.....	26	534	14
Resins, manufactured (brewers' and shoemakers' pitch, etc.)	Pounds	Pounds	Pounds
	23,590	436,730	16,530
Soap:			
Common, in bulk; in lumps, cakes, etc.; soft soap.....	253,310	1,298,300	1,601,650
Germany.....	34,610	1,235,690	1,045,210
Russia.....	440		300,490
France.....	112,440	48,720	10,360
Other (toilet, medicinal, special soaps).....	60,410	49,160	242,730
Soap powder and preparations for laundries.....	265,220	125,220	447,540
Soap waste.....	2,186,540	315,480	488,550
Starch gum, preparations for sizing and finishing.....	97,000	117,730	109,130
	Metric Tons	Metric Tons	Metric Tons
Sugar, raw and refined; glucose, solid.....		101	
	Pounds	Pounds	Pounds
Tar.....	36,150,740	1,039,480	266,620
France.....	8,007,630	51,370	31,970
Germany.....	27,925,730	982,600	220
Turpentine, spirits of.....	69,450		220

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coordinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single column of **THIS JOURNAL**, or less frequently to double column width.

Authors are requested to follow the **SOCIETY'S** spellings on drawings, *e. g.*, sulfur, per cent, gage, etc.

An Application of the Vapor Pressures of Potassium Compounds to the Study of the Recovery of Potash by Volatilization^{1,2}

By Daniel D. Jackson and Jerome J. Morgan

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

The immense amount of work which has been done upon the extraction of potash from complex mineral silicates is clearly shown by a bibliography on the subject published at the beginning of 1918 by E. C. Buck.³ This bibliography refers to no less than one hundred and thirty patents and fifty general articles published in the six years, 1912 to 1917. Of the proposed processes for the recovery of potassium in the form of soluble salts from the natural potassium-bearing silicates fully one-third are based upon the separation of the potassium compounds by volatilization. In spite of this great amount of work and with the stimulus of the inflated prices of potassium compounds, only a very few of the numerous processes proposed have been put into actual operation on a commercial scale. It was decided, therefore, to apply the knowledge obtained from the vapor pressure experiments recorded in a previous paper⁴ to an investigation of the volatilization of potassium compounds

from mixtures of silicates with releasing and volatilizing agents. It was thought that this investigation would show the reason for the apparent failure of so many of the proposed methods and might suggest the conditions for a method which would be commercially successful. In the light of the vapor pressure determinations the methods involving the use of a chloride seemed to be most practicable, and glauconite, or greensand, was thought to be the most promising of the natural silicates containing potassium. Hence the first experiments were made with mixtures of greensand and calcium chloride.

VOLATILIZATION OF POTASH FROM MIXTURES OF GREENSAND AND CALCIUM CHLORIDE

In these experiments a carefully weighed amount of greensand, powdered to pass a 200-mesh sieve, was well mixed in a small platinum boat with approximately 10 per cent of its weight of powdered, anhydrous, C. P. calcium chloride. The boat and contents were heated in the vapor pressure apparatus in a current of nitrogen dried with calcium chloride, as has been described under the determination of the vapor pressure of potassium chloride.

Irregular results obtained at 1200° C. were thought

¹ Received December 20, 1920.

² Part of a thesis submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York, N. Y.

³ *Met. Chem. Eng.*, 18 (1918), 33, 90.

⁴ Jackson and Morgan, *THIS JOURNAL*, 13 (1921), 110.

to be due to the temperature being too low for complete fusion and rapid intermingling of the reacting substances. At 1300° the results of duplicate determinations agreed better, and the amount of potassium chloride volatilized varied with changes in the speed of the gas stream in such manner that it was possible to plot the partial pressures and obtain the vapor pressure of potassium chloride in the mixture. The value of 1.6 mm. of mercury thus obtained at 1300° bore, however, no apparent relation to the known vapor pressure of potassium chloride or to the amount of potassium in the mixture. The percentage of K₂O volatilized at 1300° was found to be only slightly greater than at 1200°. On account of the claim of Spackman and Cornwell¹ that the presence of water vapor in a cement kiln aids in the formation of soluble potassium compounds from potassium-bearing silicates and acid-forming gases, *e. g.*, chlorine from the decomposition of chlorides added with the charge, experiments were made in which water vapor was mixed with the nitrogen used in the vapor pressure tube. The results of these experiments show plainly that no advantage in the formation and volatilization of potassium chloride is gained by the use of water vapor with a mixture of calcium chloride and greensand.

The figures obtained with mixtures of greensand and calcium chloride are given in Table I.

TABLE I—VOLATILIZATION OF POTASH FROM MIXTURES OF GREENSAND AND CALCIUM CHLORIDE

Expt. No.	Minutes	Temperature ° C.	Weight of Greensand	Charge CaCl ₂	Charge	K ₂ O in Residue	Per cent K ₂ O Volatilized
82	12	1204	0.5993	0.060	0.0363	0.0320	12
83	12	1203	0.6744	0.075	0.0408	0.0354	13
84	14	1208	0.6153	0.061	0.0373	0.0332	11
85	14	1205	0.5710	0.064	0.0346	0.0301	13
86	16	1201	0.7117	0.072	0.0431	0.0385	11
87	15.5	1202	0.6660	0.066	0.0403	0.0350	13
88	18	1303	0.6364	0.065	0.0386	0.0319	17
89	11	1301	0.6008	0.061	0.0364	0.0310	15
90	11	1300	0.6086	0.061	0.0369	0.0313	15
91	18	1301	0.6314	0.065	0.0383	0.0317	17
92	26	1302	0.5819	0.058	0.0353	0.0286	19
93	26	1302	0.5879	0.059	0.0356	0.0284	20
94	26	1297	0.5541	0.055	0.0336	0.0281	16
95	26	1303	0.5728	0.057	0.0347	0.0277	20
96	16	1298	0.6059	0.061	0.0367	0.0311	15
97	17	1302	0.5900	0.059	0.0358	0.0306	14
98	12	1299	0.6235	0.062	0.0377	0.0310	18
99	12	1301	0.6338	0.063	0.0384	0.0333	13

¹ The gas used was a mixture of nitrogen and dry steam.

VOLATILIZATION OF POTASH FROM MIXTURES OF SILICATES WITH LIME

The next experiments were with calcium oxide as a releasing agent. On account of the number of experiments necessary to obtain results which can be plotted and extrapolated to vapor pressures, and on account of the difficulty in finding any definite relation between the vapor pressures of potassium compounds in the mixtures and the vapor pressures of the pure compounds involved, it was decided to run the experiments in duplicate. The speed of the gas stream was varied, but the time of the experiment was kept constant. The results were expressed in terms of the percentage of potassium oxide volatilized. The knowledge of the vapor pressure of the pure potassium compounds involved was then used in interpreting the results. In the experiments with lime as a releasing agent the mixtures given in Table II were

used. The results of heating these mixtures for 11 min. at 1300° C. are shown in Table III.

TABLE II—MIXTURES OF SILICATES AND LIME USED IN VOLATILIZATION EXPERIMENTS

Mixture No.	Materials Used	Proportions Grams	Per cent of CaO after Heating Calculated	K ₂ O in Raw Mixture
I	Greensand	10		
	CaCO ₃ pptd.	22	64	1.90
3	Greensand	30		
	Limestone	70	50	2.38
VI	Greensand	10		
	Calcium hydroxide	15	62	2.46
VIII	Greensand	6		
	CaCO ₃ pptd.	9	48	2.42
VII	Greensand	6		
	CaCO ₃ pptd.	6	38	3.03
III	Feldspar	3		
	CaCO ₃ pptd.	9	65	3.50
V	Feldspar	3		
	Ca(OH) ₂	6	64	4.70

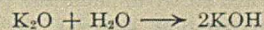
TABLE III—VOLATILIZATION OF POTASH FROM SILICATE AND LIME MIXTURES (Heated 11 min. at 1300° C.)

Expt. No.	Mixture No.	Cc. N ₂ per Min.	Water Vapor Mg.	Charge Grams	Loss in Weight Per cent	Mg. K ₂ O in Charge	K ₂ O in Residue	Per cent K ₂ O Volatilized
100	I	150	0.5754	34.9	10.9	2.7	75
101	I	117	0.5727	34.9	10.9	2.7	75
102	I	79	0.5529	35.0	10.5	2.4	77
106	I	150	10.9	0.5502	35.2	10.5	1.0	91
107	I	117	7.8	0.5695	35.2	10.8	1.1	90
108	I	80	6.0	0.5839	35.2	11.1	1.2	89
150	3	162	0.5588	32.9	13.3	9.3	30
151	3	134	0.5390	33.0	12.8	9.8	23
152	3	163	8.2	0.5242	33.5	12.5	6.1	51
153	3	132	7.2	0.5062	33.6	12.1	5.5	55
116	VI	131	0.5032	19.9	12.4	7.4	40
117	VI	135	0.4971	20.0	12.2	6.6	46
122	VI	161	13.7	0.5362	20.3	13.2	5.8	55
148	VIII	160	0.4763	30.6	11.6	10.4	10
146	VIII	160	19.9	0.4732	30.7	11.4	10.0	12
142	VII	160	0.4140	27.3	12.5	11.5	8
144	VII	160	5.8	0.4290	27.1	13.0	12.1	7
113	III	162	0.3100	34.0	10.9	9.9	9
112	III	134	0.3077	34.0	10.8	9.7	10
118	III	158	7.6	0.3030	34.3	10.6	8.5	20
119	III	133	6.6	0.3050	34.3	10.7	8.4	22
114	V	164	0.3030	17.7	14.5	13.5	7
115	V	133	0.2992	17.8	14.3	13.1	8
120	V	160	12.3	0.3262	18.1	15.7	13.5	14
121	V	146	11.1	0.3116	18.3	15.0	12.8	15

A consideration of the results of the experiments given in Table III leads to the following conclusions:

(1) The low volatilization in the feldspar mixture (III) is due to the fact that the vapor pressure of potassium oxide alone is too low at 1300° C. to cause rapid and complete volatilization of the potassium in the mixture. The vapor pressure of potassium oxide from potassium carbonate has been found to be 1.68 mm. at 970° C. and 5.0 mm. at 1130°, while the vapor pressure of potassium chloride at these temperatures is 10.1 mm. and 52.7 mm., respectively. If the vapor pressure curve for potassium oxide in potassium carbonate has the same general form as that for the chloride, the vapor pressure of the oxide at 1300° C. would be about 13 mm. It would seem that the vapor pressure of potassium oxide in the highly limed mixture of silicate and lime is not greater than that of potassium oxide in the carbonate, and has probably about the same value as the vapor pressure of water at 15° C.

(2) The explanation of the higher results in the greensand mixture (I) lies in the fact that greensand is a hydrated silicate. Accordingly, any K₂O formed by the action of CaO upon the greensand is formed in the presence of water vapor which is being evolved from the silicate. This affords an excellent opportunity for the formation of potassium hydroxide, provided the reaction



is not completely reversed at 1300° C. The statements of Deville,¹ quoted by Roscoe and Schorlemmer,² and of Watts³

¹ *Compt. rend.*, 45 (1857), 857.

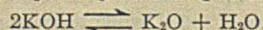
² Roscoe and Schorlemmer, "Treatise on Chemistry," Vol. II, "The Metals," 1907, 321.

³ Watts, "Dictionary of Chemistry," Vol. IV, 1868, 702.

¹ U. S. Patent 1,202,327 (1916); C. A., 11 (1917), 89.

are contradictory on this point, but it is believed that at a temperature of 1300°, or lower, the reaction of K_2O and H_2O to form potassium hydroxide must certainly take place at a speed which is not inappreciable. Now the vapor pressure of potassium hydroxide at 800° C. has been determined and found to be about as great as that of the chloride at 950° and considerably greater than that of the oxide from the carbonate at 1130°. At 1300° the vapor pressure of potassium chloride is 202 mm., and at this temperature the hydroxide must be near its boiling point. Hence it is believed that when the greensand molecule reacts with calcium oxide at the high temperature of these experiments, a considerable portion of the potassium in the greensand forms potassium hydroxide with the oxygen and hydrogen which are combined in the silicate, and is thus volatilized from the mixture. In an attempt to aid the volatilization of potassium from the greensand and feldspar before the theory of the volatilization as given above had been fully developed, some experiments were made in which calcium hydroxide was substituted for calcium carbonate in the mixtures (V and VI). The use of calcium hydroxide did not aid the volatilization and it is not to be expected that it would, for this compound is dissociated into calcium oxide and water vapor so rapidly at the high temperature of the experiments and the water vapor is so quickly carried away from the mixture by the rapid stream of dry nitrogen used that there is little chance for the formation of potassium hydroxide. On the other hand, the water vapor from greensand is given off rather slowly, and since the hydrogen and oxygen exist closely associated with the potassium in the greensand molecule there is every chance for the formation and volatilization of potassium hydroxide.

(3) The results of the experiments in which nitrogen carrying a considerable amount of water vapor was used instead of dry nitrogen confirm in a very striking manner this new theory of the volatilization of potassium from mixtures of silicates with lime in about the proportions used in the manufacture of portland cement. According to the theory, the low volatilization of potassium from the feldspar and lime mixtures is due to the low vapor pressure of potassium oxide formed by interaction of the potassium aluminium silicate and calcium oxide, and the higher volatilization of the potassium from the greensand and lime mixtures is on account of the high vapor pressure of potassium hydroxide, which is formed along with potassium oxide by the action of calcium oxide on the hydrated potassium iron silicate. The potassium hydroxide thus formed may be dissociated at this high temperature, possibly according to the reaction:



Hence it would be expected that a continuous and fairly large supply of water vapor in the atmosphere of the reaction chamber would prevent to some extent the dissociation of the potassium hydroxide and aid in the volatilization of potassium from the mixture. It would also be expected that the water vapor thus supplied would react to form hydroxide with the potassium oxide in the feldspar mixtures and increase the volatilization of potassium from these mixtures as well. The results of the experiments in which water vapor was used completely fulfilled these expectations, and thus confirmed the theory of the volatilization of potassium as developed above.

(4) The percentage of potassium volatilized from the mixture (3) of greensand with limestone is lower than that obtained when either precipitated calcium carbonate or calcium hydroxide was used. This is probably due partly to the lower lime content of the mixture and partly to impurities present in the limestone. Even in this mixture, however, the volatilization was doubled by the use of water vapor.

(5) The very low volatilization of potassium in the greensand mixtures (VII and VIII) is due partially to the small percentage of lime in the mixtures, but mainly to the fact that these low lime mixtures at this temperature fuse completely,

forming a glass in which the potassium is probably combined with the silica and thus dissolved in the other liquid silicates so that it is prevented from volatilizing both by being chemically combined in a rather nonvolatile compound and by being dissolved in a viscous liquid. Undoubtedly the small amount which was volatilized came off during the melting of the mixture. Naturally when potassium is held in a glassy silicate, water vapor cannot aid in its volatilization.

VOLATILIZATION OF POTASH FROM MIXTURES OF SILICATES WITH LIME AND CALCIUM CHLORIDE

From our knowledge of the vapor pressures of the compounds involved it might be predicted that better results would be obtained in the volatilization of potassium from silicate mixtures containing both lime and calcium chloride, than from mixtures of silicates with either of these compounds alone.

In the experiments to test the efficiency of calcium chloride as a volatilizing agent when used in conjunction with lime as a releasing agent, the mixtures given in Table IV were used. Both were made in proportions which would give, after heating, a residue that approached portland cement in composition.

TABLE IV—MIXTURES OF SILICATES WITH CALCIUM CARBONATE AND CALCIUM CHLORIDE

Mixture No.	Materials Used	Proportions Grams	Per cent of	
			CaO after Heating Calculated	K ₂ O in Raw Mixture
II	Greensand	10	65	1.90
	CaCO ₃ pptd.	21		
	CaCl ₂ anhyd.	1		
IV	Feldspar	10	65	3.70
	CaCO ₃ pptd.	26		
	CaCl ₂ anhyd.	2		

The results of heating these mixtures for 11 min. at 1215° and at 1300° C. are given in Table V. The experiments with the greensand mixture at 1300° were made first. Since the volatilization was practically complete at this temperature, the experiments at 1215° were performed so as to find whether the use of water vapor had any influence on the volatilization of potash from cement mixtures when used in connection with a chloride.

TABLE V—VOLATILIZATION OF POTASH FROM MIXTURES OF SILICATES WITH LIME AND CALCIUM CHLORIDE (Heated 11 Min. with 125 to 170 Cc. of Nitrogen Passing per Min.)

Expt. No.	Mixture No.	Temperature ° C.	Water Vapor Mg.	Charge Grams	Loss in Weight Per cent	—Mg. K ₂ O—		Per cent K ₂ O Volatilized
						in Charge	in Residue	
103	II	1300	0.5603	36.0	10.7	0.3	97
104	II	1300	0.5618	35.9	10.7	0.3	97
105	II	1300	0.5629	36.1	10.7	0.2	98
109	II	1300	10.9	0.5132	36.2	9.8	0.3	97
110	II	1300	12.0	0.5551	36.2	10.5	0.3	97
111	II	1300	8.1	0.5350	36.2	10.2	0.2	98
132	II	1215	0.5223	36.2	9.9	0.7	92
133	II	1215	0.5301	36.2	10.1	Trace	..
134	II	1215	7.4	0.5301	36.2	10.1	0.8	92
135	II	1215	15.6	0.5257	36.2	10.0	0.4	96
136	IV	1215	0.3249	36.8	12.0	3.5	71
137	IV	1215	0.3056	36.9	11.3	3.1	73
138	IV	1215	13.7	0.3021	36.9	11.2	2.9	74
139	IV	1215	7.3	0.3149	36.9	11.6	3.0	74

The results of the experiments on mixtures of greensand and of feldspar with both calcium oxide and calcium chloride in proportions to give a residue which has about the composition of portland cement show that:

(1) The removal of potassium by volatilization from the greensand mixture is practically complete in 11 min. at a temperature as low as 1215° C., but the volatilization of potassium from the feldspar mixture is not as complete.

(2) As might be expected, no advantage is gained by the use of water vapor when there is present in the mixture sufficient chlorine as chloride to form with the potassium of the silicate the stable compound potassium chloride, whose vapor pressure, 101 mm. at 1215° C. and 202 mm. at 1300° C., is high enough to allow of rapid evaporation.

(3) The claims made by Spackman and Cornwell¹ that the presence of water vapor aids in the formation of potassium chloride from chlorides and potassium-bearing silicates appear to be unfounded.

VOLATILIZATION OF POTASH FROM LOW LIME SILICATE-CHLORIDE MIXTURES

In the previous experiments we had learned: first, that potash is volatilized at a lower temperature and more rapidly from greensand mixtures than from feldspar mixtures; and, second, that the volatilization of potash from low lime mixtures which fuse is slight. It was surmised, however, that in the latter case the low volatilization was due rather to the fusion of the mixture than to the lack of lime to set free the potash from the silicate.

A series of experiments was therefore run using mixtures of greensand with a chloride and with limestone in much smaller proportions than the proportion of limestone used in portland cement mixtures. In these experiments the mixtures given in Table VI were used.

TABLE VI—LOW LIME GREENSAND-CHLORIDE MIXTURES

Mixture No.	Materials Used	Proportions Grams	Ratio of Greensand Limestone	Percentage of Chloride Added	K ₂ O in Mixture
5	Greensand Limestone	50 50	1:1	None	3.85
7	Greensand Limestone Sodium chloride	10 10 1	1:1	5.0	3.67
8	Greensand Limestone Calcium chloride	10 10 0.9	1:1	4.5	3.69
9	Greensand Limestone Sodium chloride	20 10 2.1	2:1	7.0	4.75
10	Greensand Limestone Sodium chloride	20 10 0.9	2:1	3.0	4.95

The results of heating these mixtures at temperatures just below those at which they start to fuse are given in Table VII.

TABLE VII—VOLATILIZATION OF POTASH FROM LOW LIME GREENSAND-CHLORIDE-LIMESTONE MIXTURES
(Air Passing at Rate of 100 to 150 Cc. per Min.)

Expt. No.	Mixture No.	Temperature °C.	Time, Min.	Ratio Greensand Limestone	Chloride Kind	Per cent	Charge, G.	Loss in Wt. Per cent	Potassium Oxide In Charge Mg.	In Residue Mg.	Per cent Volatilized
155	5	1050	60	1:1	None		0.4419	25.12	17.0	17.2	0
161	5	1170	30	1:1	None		0.4810	25.63	18.5	17.3	6
163	5	1170	30	1:1	None		0.4641	25.45	17.9	16.9	6
156	7	1050	60	1:1	NaCl	5.0	0.4434	30.09	16.3	6.0	63
157	7	1190	15	1:1	NaCl	5.0	0.4862	31.96	17.8	0.4	98
158	7	1200	15	1:1	NaCl	5.0	0.4737	31.10	17.4	1.6	91
159	7	1170	15	1:1	NaCl	5.0	0.4627	31.55	17.0	1.6	91
165	8	1170	15	1:1	CaCl ₂	4.5	0.4767	31.63	17.6	3.6	80
167	9	1170	15	2:1	NaCl	7.0	0.4222	28.00	20.0	3.0	85
171	10	1170	15	2:1	NaCl	3.0	0.4260	24.25	21.1	8.1	62

A consideration of the results given in Table VII shows that:

(1) The volatilization of potash from a 1:1 mixture of greensand and limestone without the addition of a chloride is very small at temperatures up to 1170° C. This is true even in the presence of water vapor which was used in Expt. 163.

(2) On addition of a chloride in proportion slightly greater than that calculated for the formation of potassium chloride,

the potash in greensand and limestone mixtures can be readily volatilized at temperatures slightly lower than the temperatures at which the mixtures begin to fuse. This has been shown for mixtures containing as little as one-third limestone.

(3) Sodium chloride appears to be somewhat more efficient than calcium chloride as a volatilizing agent, and when less chloride is used than the amount calculated to give potassium chloride with all of the potassium in the mixture there is a decided decrease in the volatilization.

SUMMARY

1—In the application of a knowledge of the vapor pressures of potassium compounds to a study of the volatilization of potash from silicate mixtures, a new theory involving the high vapor pressure of potassium hydroxide has been advanced to explain the volatilization of potassium from silicate and lime mixtures. This theory is supported by the fact that greensand which contains the elements of water loses its potassium by volatilization very much more readily than feldspar, and by the fact that when water vapor is present to aid in the formation of potassium hydroxide, the volatilization of potassium from high lime mixtures is greatly increased in every case.

2—Experiments on a mixture of feldspar with calcium chloride and lime in the proportions necessary to give a portland cement clinker, and on a mixture of glauconite with lime and calcium chloride, show that the potash is volatilized from both silicates at temperatures as low as 1215° C. The potash is, however, more readily volatilized from the glauconite than from the feldspar.

3—It has been shown that when a chloride is used in the volatilization of potash no advantage is gained by the use of water vapor. This is in accord with what might be expected, since the chloride of potassium is so much more stable at high temperatures than the hydroxide, and is contrary to the patent claims of Spackman and Cornwell.

4—Experiments on mixtures of greensand with a chloride in the proportion calculated to give potassium chloride and limestone in proportions much lower than those used in portland cement mixtures show that the potash can be readily volatilized from mixtures containing as little as one-third of limestone, provided the mixture is heated at a temperature slightly below its fusing point.

Examination for Pyrotechnic Assistant

The United States Civil Service Commission has announced an examination for pyrotechnic assistant at \$1872 a year to fill a vacancy at Picatinny Arsenal, Dover, N. J., and other vacancies requiring similar qualifications. The duties of the appointee will be to assist in the development of design, test, and manufacture of military pyrotechnics and in addition the duties of an observer and firer from aircraft. Competitors will be rated on (1) physical ability, 40; (2) education, experience, and fitness, 60. Applicants must be high school graduates and have had one year's experience along the line of pyrotechnic material. Experience in flying and acquaintance with the present equipment and devices of the Aircraft Divisions of the War Department are desirable. Applications should be filed with the United States Civil Service Commission, Washington, D. C., prior to the hour of closing business on April 5, 1921.

¹ Loc. cit.

Possible Uses of Corncob Cellulose in the Explosives Industry^{1,2}

By L. G. Marsh

PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, PITTSBURGH, PA.

Among the many economic and industrial problems arising out of the late war was that occasioned by the shortage of cotton cellulose for use in the manufacture of guncotton. The extreme importance of this problem caused a search for cotton substitutes to be instituted,³ with the hope that some material could be found suitable for use either alone or in conjunction with cotton cellulose as a basis for cellulose nitrate explosives.

PREVIOUS WORK ON COTTON SUBSTITUTES

Various forms of cellulose have previously been proposed for the preparation of nitrates, in an endeavor to produce more stable and less expensive esters, and, as early as 1859, J. Mackintosh and G. Rhodes⁴ succeeded in nitrating white pine sawdust to a constituency suitable for use as a waterproofing material.

In 1870, Henry Spill attempted to use esparto grass, but his experiments were never completely successful, owing to the difficulty encountered in the removing of the silica from the raw product.

Ramie,⁵ flax, and esculapius weed⁶ have also been investigated, and their nitrates have been successfully worked up into plastics for dental plates.

Dean prepared nitrodextrin⁷ by treating bleached cotton with sulfuric and hydrochloric acids and nitrating in the usual manner.

Bernstein⁸ made an investigation of the solid fruits, nuts, and shells of trees of the palm species, particularly the fruit of the *Phytelephas macrocarpa* (usually known as vegetable ivory) and of several species of *Mauritia*, and found that after being subjected to boiling in alkaline solutions, followed by a thorough washing in water, these materials reacted with mixtures of nitric and sulfuric acids to form esters resembling those of cellulose nitrate.

Dolliak⁹ prepared a cellulose nitrate with a nitrogen content of 11.07 per cent and a flash point of 177° C. by boiling rye straw for 15 hrs. in a 0.5 per cent caustic soda solution and then subjecting it to the action of nitrating acids.

Cross and Bevan¹⁰ carried out extensive investigations on jute fiber, and successfully established the fact that it is a mixture of cellulose and noncellulose, and yields explosive nitrates, of which the highest is the tetra nitrate. These nitrates closely resembled those of cotton cellulose in all essential points.

The Marsden Company¹¹ found that vegetable pith, such as that of maize or cornstalk, after being separated from the wood and fiber, could be nitrated successfully to an ester of great solubility and low viscosity.

Among other materials which have at various times been investigated as possible sources for commercial cellulose are wood

fiber,¹ esparto,² hemp,³ gorse,⁴ the fiber of *Ulex europaeus*,⁵ wood pulp,⁶ the flower stems of various species of agave,⁷ bamboo fiber and certain bast fibers growing in Japan,⁸ and marine fiber or *Posidonia australis*. With the exception of marine fiber and wood pulp these materials have been found to be impractical for commercial use, owing to the difficulty in purification or in obtaining sufficient amounts of the raw material to justify continued use.

Woodbridge in his investigation of wood pulp showed that this product could be used commercially as a basis for nitrate explosives, but the efficiency of its application was greatest when it was used in mixtures with cotton cellulose.

Smart,⁹ prompted by the unsuccessful cultivation of cotton in Australia and the attendant shortage of the raw product for explosive use, investigated the possibilities of marine fiber (*Posidonia australis*) as a successful source of cellulose for guncotton. The results of this investigation have shown that a stable guncotton can be produced from the fiber and the raw material can be purified on a commercial scale so as to render it suitable for nitration. Further research on a commercial scale is necessary before industrial exploitation of this material should be undertaken.

CELLULOSE FROM CORNCOB

LaForge and Hudson¹⁰ showed that corncobs, which have always been comparatively a waste product of our agriculture, can be successfully utilized as a source of raw material in the preparation of adhesive gums, crystalline xylose, acetic acid, and crystalline glucose. According to their procedure, crude cellulose was obtained as a by-product in the manufacture of xylose and adhesives as follows:

The coarsely broken corncobs were heated in an autoclave to 140° C., then at 160° C., for 1 hr., after which treatment the mixture was subjected to strong pressure to separate the liquid from the solid residue. The solution, after evaporation, constituted the adhesive gum. The solid residue remaining was heated in an autoclave with 1.75 per cent sulfuric acid at 130° C. for 1 hr., thereby causing the liberation and solution of xylose and acetic acid. After this treatment, the solid residue consisted chiefly of crude cellulose, and could be separated from the acid solution by compression.

The crude cellulose thus obtained is a rather finely divided, short-fibered, compact substance which can be readily purified. LaForge and Hudson utilized it in the preparation of glucose, and in addition to its use in the manufacture of materials necessarily characterized by a cellulose base, suggested the possibility of its use as an absorbent for nitroglycerin in dynamite.

¹ Received December 7, 1920.

² Published by permission of the Director, U. S. Bureau of Mines.

³ This investigation was undertaken by the Explosives Chemical Laboratory of the Bureau of Mines, at the request of the Committee on Explosives Investigations of the National Research Council.

⁴ Brit. Patent 734 (1859).

⁵ L. Dietz and B. P. Wayne, U. S. Patent 133,969 (1872).

⁶ Bickford, Spooner and Pyroxylin Manufacturing Co., Brit. Patent 1170 (1873).

⁷ Brit. Patent 2226 (1881).

⁸ Brit. Patent 12,778 (1885).

⁹ J. Soc. Chem. Ind., 4 (1885), 366.

¹⁰ J. Chem. Soc., 38 (1880), 667; 55 (1889), 202.

¹¹ Brit. Patent 6656 (1889).

¹ W. Ruckteschell, Brit. Patent 4349 (1885).

² Proc. Chem. Soc., 1894, 89, 137; Cross and Bevan, J. Chem. Soc., 33 (1880), 667.

³ C. F. Hengst, Brit. Patent 13,656 (1888).

⁴ A. Bouret and A. B. Verbiere, Brit. Patent 24,768 (1898); F. G. Horteloup, Fr. Patent 347,353 (1904).

⁵ G. Horteloup, Fr. Patents 331,176 (1903); 347,533 (1904); 327,136 (1902).

⁶ Brit. Patent 336 (1891); Woodbridge, THIS JOURNAL, 12 (1920), 380.

⁷ Brit. Patent 21,505 (1905).

⁸ N. Nishida, THIS JOURNAL, 8 (1916), 1096.

⁹ Chem. Eng. Min. Rev. Australia, 10 (1918), 380.

¹⁰ THIS JOURNAL, 10 (1918), 925.

CORNCOB CELLULOSE AS AN ABSORBENT FOR NITROGLYCERIN

The corncob cellulose used in the experiments was furnished to the Explosives Chemical Laboratory by the Carbohydrate Laboratory of the Bureau of Chemistry. It was prepared by the extraction of ground cobs with 1 per cent caustic soda solution at 100° C., with subsequent washing and extraction with 4 per cent sulfuric acid at 100° C.

A portion was broken up in an agate mortar and screened to pass 30 mesh, then dried at 90° C. for 5 hrs. To 9.2 g. were added 26.2 g. of nitroglycerin, the mixture well kneaded and allowed to stand for 24 hrs. Two portions of this material were then placed in Gooch crucibles and submitted to the exudation test by centrifuging.¹

The loss in weight was noted, and the material allowed to stand for an additional 24 hrs., and again centrifuged. The second loss was noted, and the residue extracted with ether in the Wiley apparatus. This extraction showed that the cellulose held 150 per cent of its own weight of nitroglycerin. This was verified by making up a mixture of 1 part of the cellulose with 1.5 parts of nitroglycerin, and testing as before. The exudation was well within the limits of safety, showing that this material could be used as a carbonaceous combustible absorbent in a dynamite.

CORNCOB CELLULOSE AS A SUBSTITUTE FOR SHORT-FIBERED COTTON IN PRODUCTION OF CELLULOSE NITRATES

In the nitration of cotton it is desirable to know the relative rates at which the cotton tested will take up the mixed acids during the nitrating process. The rates of acid absorption are naturally dependent on the purity of the cellulose material. Cotton which is free from oils and natural impurities is very readily acted upon by nitrating acids, while, in the case of the crude material contaminated with oils and other vegetable matter, there seems at first to be a repulsion between the fiber and the surrounding liquids. The absorptive power of any cellulose may be determined by a study of its action with respect to water.

ABSORPTIVE CAPACITY FOR WATER—As a preliminary step to the nitration of corncob cellulose, the rate of absorption of water was determined on the material both in its original form and after its subsequent treatment with sodium carbonate solution. The method given by Dr. C. E. Munroe² was followed. Samples of the material were dropped on the surface of distilled water, and the time from the moment that the cellulose touched the surface of the water until it became completely submerged was noted. All samples were submerged in less than 12 sec.

Similar determinations were made for the cotton to be nitrated for comparison with the corncob cellulose, both in its original condition and after purification by successive boilings in 5 per cent sodium carbonate-

1 per cent bleaching powder solution and water, following the identical treatment described for the purification of the corncob cellulose. The unpurified cotton was not submerged in 24 hrs., while the purified samples were submerged in 1.5 min. These results indicate that corncob cellulose will be very readily acted upon by nitrating acids.

NITRATION—The nitrating acid consisted of mixed nitric and sulfuric acids containing 22 per cent HNO₃, 14.2 per cent H₂O, and 0.1 per cent N₂O₄. The cotton was nitrated in the usual way, the excess acid wrung out, and the cotton washed thoroughly with hot and cold water, then cut in the beater. After this it was again washed several times with hot and cold water until it proved to be stable by the Abel and 135° tests. It had a nitrogen content of 12.66 per cent and gave a yield of 151 per cent of the dry cotton.

The corncob cellulose was nitrated in the same way, but there was difficulty in separating the nitrated product from the acid. The material was so fine that it passed through the screen. It was finally separated by gravity, using a mat of nitrated cotton. It did not hold as much acid mechanically as nitrated cotton filtered in the same way. It was easy to wash, as it settled readily and the water was drawn off from the top. The material was so fine that it was not cut in the beater, but the purification was continued as in the case of the nitrated cotton.

There was no apparent difference in the results of the heat tests, as the corncob nitrocellulose met the specifications for use in smokeless powder in this respect.

The nitrogen content was only 12.30 per cent and the acetone-insoluble, or unnitrated material, very high. A sample of the nitrated cellulose was dissolved in acetone and filtered off from the insoluble residue, after which the soluble nitrocellulose was thrown out of solution and nitrogen determined. This portion ran 12.70 per cent nitrogen. On examination, the residue was found to consist of fine, hard grains, apparently little touched by the acids. Several determinations were made with acids containing more water, and with the time of nitration increased to 2 hrs., but in every case the acetone-insoluble was much too high. The hard nature of the residue, as well as the excessive amount, would make it impossible to use this nitrocellulose in the manufacture of a perforated powder.

Some experiments were conducted to overcome the mechanical losses due to the fine material remaining with the acid. Mixtures of equal parts of cotton and corncob cellulose were nitrated together. The longer fibers of cotton acted as a mat and held most of the corncob nitrocellulose. There was little use of carrying the work further, however, as the final product did not meet the requirements in regard to acetone-insoluble residue.

The yields in the corncob cellulose averaged about 130 per cent. This was accounted for by the loss of fine material and the residue that was not nitrated, or only partially nitrated.

¹ Bureau of Mines, *Bulletin* 51, 10.

² "Inspection of Cotton for Use in the Manufacture of Gun-cotton," *J. Am. Chem. Soc.*, 17 (1895), 793.

Where a thin solution of the nitrocellulose was made by dissolving the nitrated material in a solvent such as ether-alcohol, acetone or amyl acetate, the insoluble material settled out from a clear supernatant liquid, indicating that it could be used in the manufacture of collodion and some lacquers. In these products, however, the cost of the nitrocellulose itself is of minor importance as compared with the other costs. So there is no advantage in using nitrated corn cob cellulose as long as cotton is available.

CONCLUSIONS

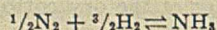
It appears that the only use for corn cob cellulose in the explosives industry at the present time is as a carbonaceous absorbent for liquid ingredients, such as nitroglycerin, in the manufacture of dynamite. For that use it must compete with such materials as wood pulp, sawdust, cornmeal, charcoal, peanut hulls, rice hulls, and similar materials, all of which have properties which are advantageous for the manufacture of special grades of dynamite.

Some Interpretations of the Ammonia Synthesis Equilibrium¹

By R. S. Tour

PLANT ONE SECTION, NITRATE DIVISION, ORDNANCE DEPT., AND THE FIXED NITROGEN RESEARCH LABORATORY, WASHINGTON, D. C.

The extent to which the reaction



can proceed is a function of the temperature, pressure, and concentrations of the components of the system. Thermodynamic considerations lead to the following relation for concentrations at equilibrium:

$$CNH_3 = K_c \times (CN_2)^{1/2} \times (CH_2)^{3/2} \quad (1)$$

where K_c is the concentration equilibrium constant. Using partial pressures instead of concentrations, the above may be expressed as:

$$p(NH_3) = K_p \times (p_{N_2})^{1/2} \times (p_{H_2})^{3/2} \quad (2)$$

where $p(NH_3)$, (p_{H_2}) , (p_{N_2}) are partial pressures in atmospheres of the respective constituents and K_p is the pressure equilibrium constant. In the latter form Haber² gives the following equation for the value of K_p as a function of the absolute temperature T :

$$\log_{10} K_p = \frac{13.100}{4.571 T} - 6.134 \quad (3)$$

If a = volume fraction of ammonia in the system at equilibrium,

c = volume fraction of inert gases at equilibrium,

r = volume ratio of hydrogen to nitrogen at equilibrium,

P = total pressure in atmospheres,

then by simple transformations we may arrive at the following relation:

$$\frac{a}{(1-a-c)^2} = KP \frac{r^{3/2}}{(1+r)^2} \quad (4)$$

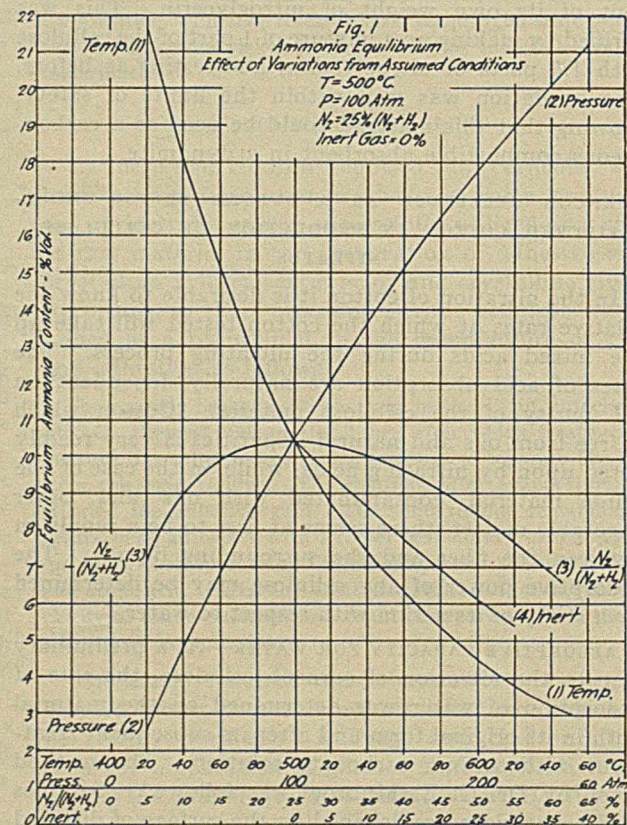
where K has the same value as K_p above.

If interested in the ammonia content, the equilibrium condition may be most simply inspected and calculated, and the effect of different variables best noted and determined with the help of Formula 4. In Fig. 1 is given a set of curves showing the effect on equilibrium ammonia content of a variation of any one of the conditions involved when the others are held at the arbitrary values: $T = 773^\circ A.$, $P = 100$ atmospheres, $r = 3$, $c = 0$. It is to be noted from the equation and the curves that:

(1) The effect of temperature is very marked, especially at the lower temperatures, the ammonia content rapidly increasing with decrease in temperature, although it should be remembered that reaction velocity decreases very rapidly with this

decrease of temperature. A reduction of temperature from 500° to $485^\circ C.$ is as advantageous as a rise in pressure from 100 to 120 atmospheres.

(2) Pressure does not increase the ammonia content in direct proportion, but at a decreasing rate with increasing ammonia content.

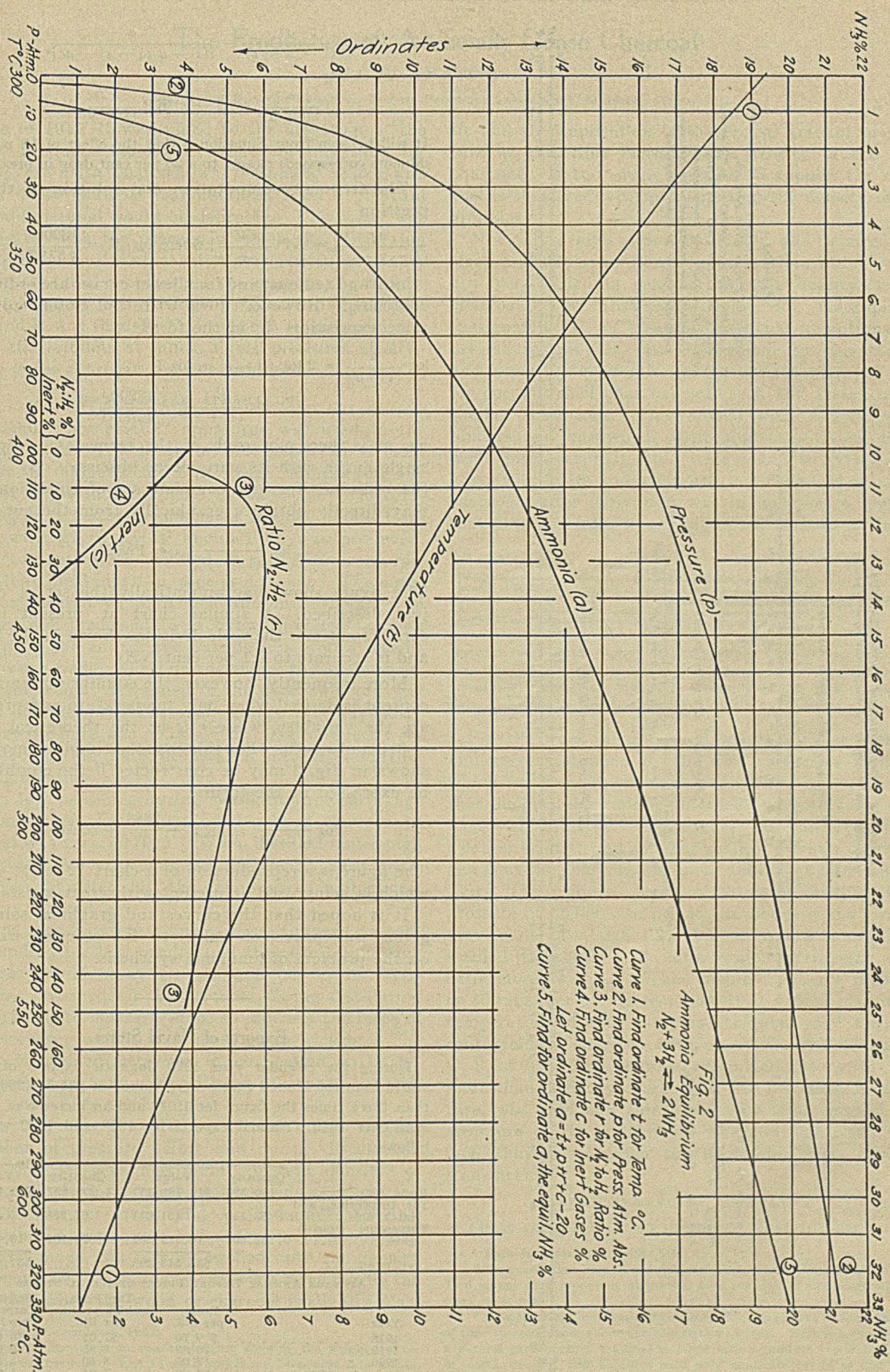


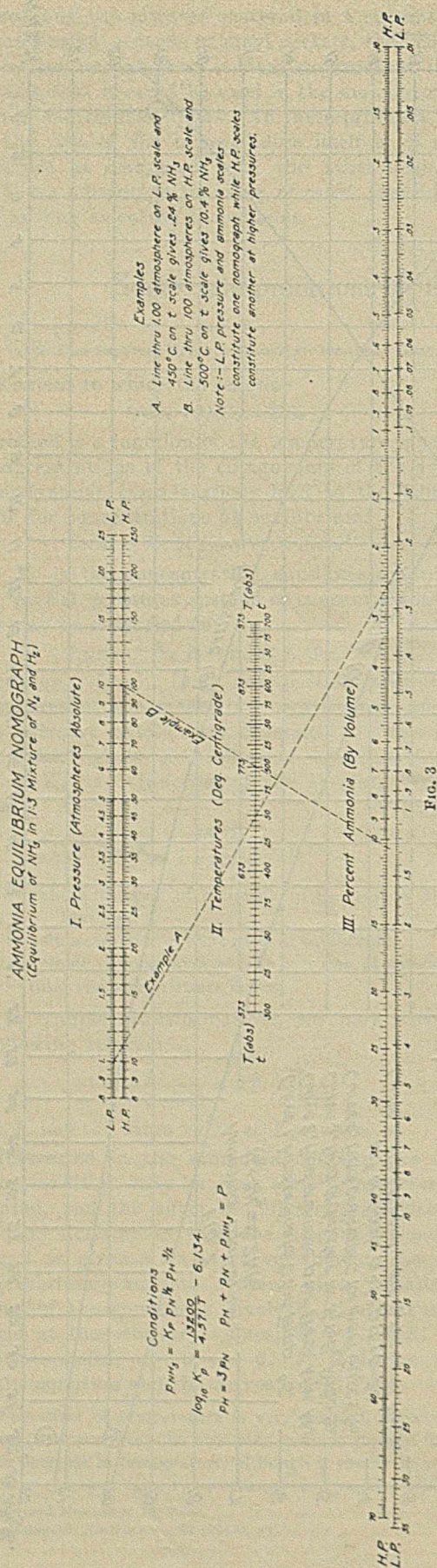
(3) Changes in ratio of hydrogen to nitrogen have but a small effect over a considerable range. The maximum ammonia content is, of course, for the theoretical proportion of $1N_2 : 3H_2$, but a variation to $2N_2 : 3H_2$ (or $0.5 N_2$ to $3 H_2$) involves a reduction of less than 10 per cent of the equilibrium content.

(4) The effect of inert diluents is often misunderstood and considered as merely similar to an equal percentage drop in pressure. It should be noted, however, that the pressure of the diluent not only lowers the partial pressures of the reacting gases, but also actually dilutes them as well. To show this we may write the equilibrium expression in the form:

¹ Received November 26, 1920.

² F. Haber, *Z. Electrochem.*, **21** (1915), 89.





$$\frac{a}{(1-a-c)^2} = \frac{a}{[(1-a)(1-c)-ac]^2}$$

or very closely

$$\frac{a}{(1-a)^2} = (1-c)^2 K_P \frac{r^{3/2}}{(1+r)^2} \quad (5)$$

It will be seen from Equation 5 that the effect of 10 per cent diluents corresponds closely to a 20 per cent drop in pressure.

The frequent computation and solution of the expression

$$\frac{a}{(1-a-c)^2} = K_P \frac{r^{3/2}}{(1+r)^2}, \text{ where } \log_{10} K = \frac{13200}{4.571 T} - 6.134$$

is long and tedious, and families of curves are ordinarily confusing. However, if we write the closely approximate expression (5) in the form:

$$\log \frac{a}{(1-a)^2} = 2 \log (1-c) + \log P + \log \frac{r^{3/2}}{(1+r)^2} + \frac{13200}{4.571 T} - 6.134 \quad (6)$$

we may then plot each of the terms as a separate single curve with its variable as abscissa. By adding the ordinates for any complete set of conditions, we may directly obtain a graphically from the curve for

$$\log \frac{a}{(1-a)^2} \quad (\text{see Fig. 2}).$$

The figure shows diagrammatically the set of curves just described. A similar chart at present in use carries ten times the scale divisions shown in the figure and is accurate to 0.1 per cent NH_3 .

More frequently, however, the equilibrium ammonia content is desired when only temperature and pressure are the variables, while r is at the theoretical value of 3.0 and $c = 0$. For this case the simple nomograph shown in Fig. 3 may be constructed if the equilibrium be expressed in the form:

$$\log \frac{a}{(1-a)^2} = \log P + \frac{2888}{T} + \text{const.} \quad (7)$$

The figure is a reproduction of a chart 12 in. \times 42 in., which is being used at present with great satisfaction.

It is hoped that the curves and graphical solutions given will prove of value to laboratories working on the problem of ammonia synthesis.

Exports of Naval Stores

During the calendar year 1920 domestic exports of naval stores from the United States were valued at \$34,545,296, more than three times the figure for 1918, and an increase of 10 per cent over 1919. Annual exports for 1919 and 1920 were as follows:

	1920		1919	
	Quantity	Value	Quantity	Value
Rosin, bbls.....	1,160,385	\$19,781,353	1,209,627	\$20,433,970
Tar, turpentine, and pitch, bbls.....	53,149	451,641	67,258	551,793
Turpentine (spirits) gals.....	9,162,607	14,312,302	10,672,102	10,448,234
TOTAL.....		\$35,545,296		\$31,433,997

AVERAGE ANNUAL EXPORT PRICES OF NAVAL STORES

Year	Rosin, per Bbl.	Tar, Pitch, and Turpentine, per Bbl.	Spirits of Turpentine, per Bbl.
1918.....	\$ 9.70	\$7.61	\$0.612
1919.....	16.89	8.85	0.979
1920.....	17.05	8.50	1.562
December 1920.....	12.30	7.04	1.089

The Production of Artificially Dense Charcoal¹

By L. F. Hawley

SECTION OF DERIVED PRODUCTS, FOREST PRODUCTS LABORATORY, MADISON, WISCONSIN

Late in 1917 it was called to the attention of the Forest Products Laboratory that coconut shell for making gas-mask charcoal was becoming scarce and that a dense charcoal manufactured from a plentiful domestic material would be desirable. The writer was acquainted with the process in which the distillation of briquetted hardwood sawdust was carried out under slight mechanical pressure for the purpose of preventing the briquets from falling to pieces during the process, and it was thought that by both making and distilling the briquets at much higher pressures an artificially dense charcoal could be produced.

SMALL-SCALE APPARATUS

A small "homemade" apparatus was used to try out this idea. The briquets were made in a mold $1\frac{15}{16}$ in. in diameter and 6 in. deep. By packing the sawdust firmly into the mold by hand and then compressing in a testing machine, a briquet about 1 in. thick, with a gravity of about 1.08, was produced. These briquets were distilled in a 2.5-in. iron pipe, 2.5 ft. long, held in a 4-in. pipe as a jacket. The outer pipe was heated by a row of Bunsen burners. The pressure was furnished by a screw threaded through the cap on the end of the outside pipe and a weight hung over a pulley wheel on the end of the screw-shaft. When the weight descended to the floor, the cord was wound around the pulley again and in this way fairly constant pressure was maintained. The briquets were separated by thin plates of metal to prevent them from sticking together.

With low pressures during distillation the shrinkage in diameter of the briquet as the wood changed to charcoal was very marked. When distilled under high pressures, however, there was frequently very little change in diameter, but the compression in thickness was very marked.

It was soon found that fine sawdust (under 20-mesh) was required for best results, and that the briquetting pressures should be at least 15 tons per sq. in. The pressures obtained on the briquets during distillation were difficult to measure, since so much of the force of the descending weight was taken up in friction. The figures mentioned hereafter in connection with this apparatus were computed with an allowance for friction of one-half of the total force.

Several species of wood were tried under varying conditions of pressure before and during distillation, and a charcoal with maximum apparent density² of 0.57 was made from maple-wood sawdust briquetted at 50,000 lbs. per sq. in. and distilled under 300 lbs. per sq. in. The briquets had a density of about 1.10 when first made, but rapidly swelled until the density was about 1.09. Apparently there is a stage during the distillation when the wood or charcoal is slightly plas-

tic and the application of the proper amount of pressure at this time increases the density of the final charcoal. If too much pressure is applied the charcoal is shattered without increasing the density of the granules.

Not only a high apparent density was required but also an absorption value after activation, which value, however, varied in general with the density of the charcoal. The absorption value for chloropicrin¹ (designated "C. P."), under standard conditions expressed in minutes, was determined for this sample and found to be 590 min., in comparison with 900 min. for coconut-shell charcoal activated and tested under similar conditions. Pine woods with natural rosin binders and hardwoods with binders of rosin, hardwood pitch, asphalt, etc., were found to give higher gravity briquets and charcoal, but the C. P. of these charcoals after activation was in no case so high as that obtained from wood briquetted without a binder.



RETORT FOR DISTILLATION OF BRIQUETS UNDER MECHANICAL PRESSURE

A—4-in. pipe; B—collars to hold pipe E in place; C—collar to increase thread length through top of cap; D—screw; E—2.5-in. pipe; F—bearing plate; G—wheel for moving screw D; H—outlet to condenser

Further work on untreated woods with or without binders was stopped by the discovery of a material which was very much more promising. It was found that the insoluble residue obtained by hydrolyzing sawdust with dilute acid and leaching out the sugar² gave a denser briquet, and a higher yield of a denser charcoal, and that the charcoal was more absorbent after activation. The briquets made of 20-mesh dust under a pressure of 35,000 lbs. per sq. in. had a gravity when first made of about 1.21, but in a few hours they swelled to about 1.18, after which there was very little more swelling. When distilled under a pressure of 300 lbs. per sq. in. (estimated) at a final maximum temperature of 450° C., these briquets gave a 40 per cent yield of charcoal with an A. D. of 0.52 and a C. P. of 700. This charcoal resembled anthracite coal³ more than ordinary charcoal; it had a conchoidal fracture, was hard and shiny, and showed no trace of the structure of the wood from which it was made. In fact, thin pieces under the microscope were slightly translucent.

SEMICOMMERCIAL APPARATUS

These results were so promising that further small-

¹ THIS JOURNAL, 11 (1919), 519.

² "Ethyl Alcohol from Wood Waste," *Met. Chem. Eng.*, 15 (1916), 78. Two plants were producing about 400 tons per day of this material and using it for fuel.

³ It is, therefore, unnecessary to assume high pressures or long periods of time to account for the natural formation of coal. Here is a case where a natural carbonaceous material is made into a product resembling coal in luster, density, and hardness with only moderate pressures and in a very short time.

¹ Received December 3, 1920.

² Apparent density is an empirical figure showing the weight per cc. of the charcoal between 8- and 14-mesh which can be poured into a tube 10 cm. long by 1.41 cm. in diameter under closely specified conditions.

scale work was considered unnecessary, and attempts were made to confirm the results in semicommercial apparatus. The Development Division of the Chemical Warfare Service finally offered to construct and operate a larger apparatus, and the rest of the work was carried on at the Defense Laboratory of that Division. A retort 10 ft. long was constructed in which 4-in. briquets could be distilled, while the pressures on the briquets could be automatically regulated at any height desired.

It was soon found that the optimum pressures as estimated from the results with the small apparatus were too high and that only about 125 lbs. per sq. in. were required for the best results. It was also found that, as might be expected, a much more careful regulation of conditions was required in the larger apparatus to obtain a satisfactory product. Even with the best regulation of the temperature that could be obtained a portion of the charcoal was unsatisfactory in density. The end surfaces of all the briquets next to the plate were hard and dense, but the center portion of some of them was porous and soft. Since it seemed that it was only the pressure conditions of the small-scale work which were not reproduced very closely in the large-scale work (except those conditions due to the size of the units), an attempt was made to reproduce the pressure conditions also. The pressure in the small-scale work was known to have been very uneven, since the weight would often remain still for a time and then drop several inches. This effect was simulated in the larger apparatus by adjusting the pressure-control apparatus so that the pressure varied over a wide range, dropping from maximum to minimum slowly and then rapidly running up to maximum again. With these pressure conditions it was possible to make a much better quality of charcoal. The best results were obtained with briquets made of medium-sized commercial hydrolyzed sawdust (between 4- and 43-mesh), distilled slowly under pressures varying from 80 to 130 lbs. per sq. in. It was not possible to make this charcoal quite so hard and homogeneous as that made on a small scale with the 2-in. briquets, but an A. D. of 0.58 on the untreated coal was obtained and a C. P. of 600. There are several possible reasons for the less satisfactory results shown by the large-scale work:

1—The actual size of the briquets may have been too large to allow a ready escape of the vapors from the center of the briquet to the surface, while at the same time the pressure was applied constantly enough to get the full effect. This might be the cause of the porous centers of some of the charcoal briquets.

2—The raw material was coarser and not so completely cooked through.

3—There was no way to obtain high pressures in making the briquets, the maximum used being only about 20,000 lbs. per sq. in.

4—No other study was made of special activation methods for this charcoal except comparative tests by the same activation methods as were used for coconut-shell charcoal. The wood charcoal having had a maximum temperature of only about 350° C., naturally contained much more volatile matter

than the coconut shell which had been distilled at 900° C., and this may have influenced the activation results.

SUMMARY

On a small scale, a charcoal was made from native raw materials which had an apparent density (A. D.) of 0.62 and an absorption value for chloropicrin (C. P.) of 700 min., as compared with a standard coconut-shell charcoal value of A. D. 0.63 and C. P. 900.

On a larger scale (commercial-sized unit) an A. D. of 0.58 and C. P. of 600 were the best that could be obtained after incomplete experimental work.

Food Research Institute

At the suggestion of Herbert Hoover, a Food Research Institute for the study of all problems of production, distribution, and consumption is to be established at Leland Stanford Junior University, with an endowment of \$700,000 provided by the Carnegie Corporation. Under the terms of the agreement, the university agrees to establish a research organization and to appoint three men of science, to be known as directors of the Institute, who will have authority to determine the scientific policies of the institute and the problems to be studied. The directors will head three separate divisions; one will be an expert in the field of physiology and chemistry of nutrition, one in economics and food distribution, and one in the chemistry of food manufacture and agriculture. There will also be an advisory committee made up of men of national prominence (among them being Mr. Hoover), representing agricultural, consumer, economic, and other groups of the community. The university will appoint seven members, the president of the university and the president of the Carnegie Corporation serving ex-officio. It is the hope of the Carnegie Corporation that eventually the new organization will be known as the Hoover Institute. The institute may receive such specially qualified students as it may be possible to instruct without disadvantage to the primary research purposes of the organization. A small group of fellowships will be available for graduate students. The institute will begin its work July 1, 1921, the Carnegie fund being provided for a period of ten years. After the institute is once established, the Carnegie Corporation will abstain entirely from any direction or control of the work.

Classification of Coal for Export

A cooperative agreement has been effected between the Tidewater Coal Exchange, Inc., of New York and the U. S. Bureau of Mines for the classification of coal shipped for export through the ports of New York, Philadelphia, and Baltimore on a basis of accurate sampling and analysis. The agreement provides for the establishment of limits and tolerances of quality for certain pools and for the maintenance of the quality of the pools within the limits specified. The Bureau of Mines will direct the work of obtaining the technical information required, collecting representative samples of coal as shipped and of mine samples when necessary and making analyses at the Pittsburgh Experiment Station. The Tidewater Coal Exchange will make classifications on a basis of the analyses and will assign coal to pools within the limits and tolerances as finally published. The general purpose of this classification is to expedite transportation and shipment and to insure the maintenance of certain standards as representative of the quality of American coals shipped from various districts to Europe. The pooling of coals was resorted to in war time by a voluntary organization of coal operators and railroads, and in view of the great saving in the use of freight cars and maritime shipping it has been found desirable to continue the arrangement.

The Melting Point of Ammonium Sulfate¹

By James Kendall and Arthur W. Davidson

CHEMISTRY DEPARTMENT, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

The implicit trust which most chemists place in tables of constants is unfortunately not always justified. Even for the most common chemicals, the current data for such fundamental properties as melting point and boiling point are often quite indefinite. For example, the melting point of potassium iodide² is variously given as from 614° to 723°. For the melting point of ammonium sulfate, a substance which is produced by the ton daily, the figures fluctuate still more widely. The lowest recorded value is 140°, the highest 423°; truly a remarkable variation in a simple physicochemical "constant!"

This particular case is cited by a recent writer³ as "a striking example of the neglect of physical chemistry in Germany;" his own efforts to furnish a solution, however, only serve to confuse the problem still further. To enable us to escape the possible reproach that physical chemistry is still more flagrantly neglected in this country, a brief discussion of the fusion phenomena of ammonium sulfate and an explanation of the discrepancies in the literature may be here presented. For a more detailed examination of the system: ammonium sulfate-sulfuric acid, reference should be made to a recent article by Kendall and Landon.⁴

PREVIOUS INVESTIGATIONS

The results of previous investigators may first be summarized. Marchand⁵ in 1837 obtained a melting point of 140°, which has been handed down ever since in all the textbooks and tables as the melting point of the neutral salt. After more than 80 years, however, it has been discovered⁶ that the work of Marchand, owing to his rather misleading method of expression, has been misinterpreted, 140° referring not to the neutral salt, $(\text{NH}_4)_2\text{SO}_4$, but to the acid salt, NH_4HSO_4 . Hodgkinson and Bellairs⁷ described the use of dried and carefully melted ammonium sulfate in 1895, but gave no value for the melting point. The objection was immediately raised by Smith⁸ that neutral ammonium sulfate does not melt when heated, but decomposes with loss of ammonia, leaving finally the acid salt, which melts at 146°. This was confirmed by Reik⁹ in 1902 and by Langmuir¹⁰ in 1920. Bridgman¹¹ has reported that acid ammonium sulfate is "entirely melted" at 150°, but gives no minimum value. Kendall and Landon obtained $146.9 \pm 0.5^\circ$ as the melting point of the acid salt, but did not succeed in melting the neutral salt in a sealed tube even at the boiling point of sulfur. Caspar¹² states that the neutral

salt sinters in an open tube at about 310°, melts at 336° to 339°, and decomposes at 355° with evolution of gas; in a closed tube it sinters at about 360° and melts at 417° to 423°. Jänecke,¹ finally, in an ambitious attempt to define the essential features of the complete phase-rule diagram for the system $\text{H}_2\text{SO}_4\text{--NH}_3$, claims to have obtained 251° for the melting point of the acid salt and 357° for the simultaneous melting and decomposition points of the neutral salt under atmospheric pressure.

The essential source of the divergent values obtained is the instability of the neutral salt. All investigators agree that the acid salt NH_4HSO_4 is quite stable at its melting point; Jänecke even gives it a definite boiling point of 490°, a figure which, in view of the dubious character of his remaining results, must be regarded with considerable reserve. Kendall and Landon's carefully determined value for the melting point of the acid salt (146.9°) is in very good agreement with the results of all previous observers; how Jänecke could possibly obtain a figure more than 100° higher (251°), unless he misread his thermometer by 100°, must remain a mystery. The neutral salt, however, loses ammonia when heated, decomposition being appreciable² even at 200°. When the neutral salt is heated in an open tube, therefore, the determination of a true melting point is impossible, since the composition of the solid phase is changing from minute to minute through loss of ammonia. If this ammonia is allowed to escape freely and the experiment persisted in long enough, the melting point of the acid salt will finally be obtained. If, on the other hand, the apparatus is so arranged that the ammonia evolved is permitted to accumulate above the salt, decomposition will cease before the acid salt is reached. Thus, Smith found that when dry NH_3 gas was bubbled through melted NH_4HSO_4 considerable absorption took place even at temperatures as high as 420°. The ammonia so taken up was evolved again, however, on passing a current of air through the apparatus, even at temperatures as low as 200°. It is obviously futile, consequently, to speak of determining the melting point of neutral ammonium sulfate under atmospheric pressure. This statement holds even if a pure ammonia atmosphere is ensured, for while it is true that the mixture of neutral salt and acid salt³ obtained on heating will possess a definite vapor tension with respect to ammonia at any fixed temperature, and at some fixed temperature will melt, yet it could only be by an extreme coincidence that fusion should take place at that very temperature for which the vapor tension just equals one atmosphere and (as will appear below) the coincidence does not occur in practice in this particular case. The values 336° and 357°

¹ Loc. cit.

² Smith, Loc. cit.

³ It may be mentioned here that the existence of salts intermediate in composition between the neutral salt $(\text{NH}_4)_2\text{SO}_4$ and the acid salt NH_4HSO_4 (see Kendall and Landon, Loc. cit.) necessitates the decomposition taking place in stages, and not directly.

¹ Received February 2, 1921.

² Kaye and Laby, "Physical and Chemical Constants," 1911, 115.

³ Jänecke, Z. angew. Chem., 33 (1920), 278.

⁴ J. Am. Chem. Soc., 42 (1920), 2131.

⁵ Pogg. Ann., 42 (1837), 556.

⁶ Caspar, Ber., 53 (1920), 821.

⁷ Proc. Chem. Soc., 152 (1895), 114.

⁸ J. Soc. Chem. Ind., 14 (1895), 629.

⁹ Monatsh., 23 (1902), 1033.

¹⁰ J. Am. Chem. Soc., 42 (1920), 282.

¹¹ Proc. Am. Acad. Sci., 52 (1916), 125.

¹² Loc. cit.

obtained by Caspar and Jänecke, respectively, for the melting point of neutral ammonium sulfate heated in open tubes must, therefore, refer to perfectly indeterminate mixtures, not in equilibrium with their vapor phase. For the same reason the elaborate phase-rule diagram presented by Jänecke is hopelessly in error, as may be seen by comparing it with the results obtained by Kendall and Landon with the use of sealed tubes.

The actual melting point of neutral ammonium sulfate can, indeed, be determined only by heating the salt in a sealed tube with practically no free air space, to avoid appreciable loss of ammonia. It is true that a melting point so obtained refers to a pressure in excess of atmospheric, but the temperature of the equilibrium solid-liquid changes in general so slightly,¹ except for tremendous pressure variations,² that this is of no practical significance.

The only definite value reported for the melting point of neutral ammonium sulfate in a sealed tube is that of Caspar, 417° to 423°. In view of the fact, however, that Kendall and Landon failed to obtain a melting point for a specimen of the salt suspended in a sealed tube in the vapor of boiling sulfur (445°), it would seem that Caspar's determination is doubtful. The most probable explanation is that considerable decomposition of the salt occurred before fusion, owing to the air space in the sealed tube being too large, thus inducing too low a value for the melting point. The experiments described below conclusively prove that Caspar's result is in error.

EXPERIMENTAL PART

A pure sample of the salt was obtained in the form of very fine crystals by rapid cooling from a concentrated hot aqueous solution, which was well stirred during the precipitation. The crystals were washed with alcohol and ether successively, and desiccated over 99 per cent sulfuric acid. Small glass bulbs of the type shown in the diagram were packed with the crystals and then sealed off at the point A, leaving as small an air space as possible. A sealed bulb was attached to a nitrogen-filled thermometer (reading to 560°) and suspended in a Pyrex test tube containing powdered anhydrous zinc chloride. This tube was air-jacketed with larger tubes and finally with a beaker, the whole being surrounded by sheet asbestos, with glass windows for observation. The temperature was raised very gradually by means of a number of Bunsen burners to about 550°, the crystals thus being brought to their fusion point in a bath of molten zinc chloride.

The first tubes, made of thin glass, exploded before the salt showed any signs of melting. Later attempts were consequently conducted with bulbs made from thick-walled capillary tubing, with better success. Two concordant experiments gave melting points of 520° ±

¹ For the mean case, an increase of pressure of more than 30 atm. is required to produce a change in the melting point of 1°. See Findlay, "The Phase Rule," 1918, 71.

² Bridgman, *Proc. Nat. Acad. Sci.*, 1 (1915), 514.

5°, but in view of the smallness of the bath and the uncertainty in the exposed stem correction for the thermometer, this value was regarded as only approximately accurate. The salt showed signs of softening below 500°.

The final experiments were carried out with a much larger bath (a one-liter Pyrex beaker, thoroughly insulated with asbestos and provided with observation windows, containing a mixture of fused nitrates stirred by means of a motor-driven brass stirrer) and a calibrated platinum resistance thermometer.¹ The temperature of the bath was allowed to rise exceedingly slowly (not more than 0.2° per min.) in the neighborhood of the melting point. The salt began to soften perceptibly at 490° and finally melted at 513° ± 2°. This value may, therefore, be given as the definite melting point of neutral ammonium sulfate, under an ammonia pressure of considerably more than one atmosphere.²

High as this figure may appear in comparison with the results of previous investigators, it is of interest to note that it is still far below that recently predicted by Langmuir.³ According to the octet theory of valence, the melting point of ammonium sulfate should be only a little below that of potassium sulfate (1072°); in reality it is more than 500° lower. We have here, indeed, the first known example of an inorganic sulfate with a melting point below that of the corresponding chloride. Langmuir, by the use of the same method as was employed in this work, has lately determined the melting point of ammonium chloride as 550°, under an estimated pressure of 66 atmospheres. The difference between this value and that here obtained for ammonium sulfate is not very large, but it is significant, since all other sulfates melt at temperatures considerably higher than the corresponding chlorides.

SUMMARY

Jänecke recently pointed out the fact that the melting point of ammonium sulfate is not accurately known, and attempted to remedy the deficiency.

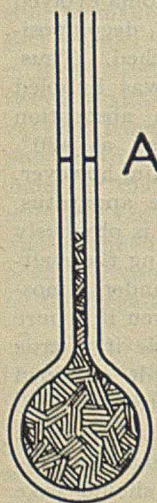
It is demonstrated in this article that Jänecke's value for the melting point of *acid* ammonium sulfate (251°) is more than 100° too high, the correct figure being 146.9° ± 0.5°, while his value for the melting point of *neutral* ammonium sulfate (359°) is more than 150° too low, the correct figure being 513° ± 2°. The extreme discrepancies recorded in the literature are shown to be due essentially to the instability of the neutral salt when heated in an open tube.

In the light of the results here obtained, it would seem that Jänecke's plea for more investigations of the physical properties of the common chemicals in everyday use might profitably be amended to a plea for fewer investigations, of somewhat greater accuracy.

¹ For the use of this apparatus we wish to express our thanks to Professor C. D. Carpenter.

² Since some loss of ammonia must have occurred before the salt melted, the value here determined is, strictly speaking, only a minimum figure. In view of the small air space left in the sealed tube, however, we feel confident that any change in composition of the salt before melting, and consequently any error in the melting point recorded due to this cause, cannot be appreciable. The only factor that might introduce any significant error is the solvent action of the partially molten ammonium sulfate on the glass, which was quite noticeable, but unavoidable under the conditions of experiment.

³ *J. Am. Chem. Soc.*, 42 (1920), 282.



Rapid Dry Combustion Method for the Simultaneous Determination of Soil Organic Matter and Organic Carbon¹

By J. W. Read

DEPARTMENT OF AGRICULTURAL CHEMISTRY, ARKANSAS EXPERIMENT STATION, FAYETTEVILLE, ARKANSAS

In order to carry out certain investigations on the quantitative relations of soil organic matter it became necessary to devise an accurate and suitable procedure for determining the percentage of carbon in the organic matter in a large number of representative soils selected from nearly every Experiment Station in the United States for the purpose of making a more exact study of the percentage relationship of the organic carbon to the total organic matter. The methods in general use for the total organic matter determination are (1) the loss on ignition, and (2) the organic carbon method. The latter involves the use of a conventional conversion factor.

A scheme which would make it possible to determine the organic matter and the organic carbon simultaneously, thereby reducing the labor to about one-third, at the same time securing the highest accuracy, was the chief object sought. The method described below met these requirements the most satisfactorily. By its use the writer was able to complete twelve combustions, twenty-four determinations, in an ordinary day's work, including all the necessary preliminary and final weighings, and employing only one combustion furnace. With the exception of several modifications and the introduction of a new feature in the type of combustion boat, the rapid organic combustion method as modified and used by Levene and Bieber² formed the basis of the procedure adopted. The success of determining on the same sample of soil both the organic matter and the organic carbon simultaneously is due in the main to the use of a special perforated-bottom combustion boat³ and a specially constructed filter funnel,⁴ which made it possible to filter by suction in the same manner as with the ordinary Gooch crucible. The boat possessed suitable dimensions (97 mm. long, 18 mm. wide, 13 mm. deep) for handling the quantity of materials required.

One-gram samples of soil (1-mm. sieve) were prepared for combustion by removing the carbonates and hydrated minerals in accordance with Method B described by Rather.⁵ This preliminary preparation may be briefly stated as follows:

A 1-g. sample of soil is weighed into a platinum evaporating dish and given six successive digestions, 5 min. each, on a boiling water bath, with 30 cc. of water and 10 cc. each of 2.5 per cent hydrochloric and hydrofluoric acids. After each digestion the supernatant liquid is carefully decanted through the combustion boat on to an asbestos mat. After the sixth digestion the entire sample is transferred to the boat with a rubber policeman.

¹ Presented before the Division of Agricultural and Food Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

² *J. Am. Chem. Soc.*, **40** (1918), 460.

³ Made especially by the Coors Porcelain Co., Golden, Colorado. The writer sincerely thanks the company for the valuable cooperation given him and for the care and pains taken to produce a satisfactory boat.

⁴ Grateful acknowledgment is made to Eimer and Amend for their construction of the special filter funnel used with the boat. (See Fig. 3.)

⁵ Arkansas Experiment Station, *Technical Bulletin* **140** (1917); *This Journal*, **10** (1918), 439.

The results reported by Rather indicate that the amount of organic carbon lost in the filtrate from the acid treatment is negligible, falling within the limit of error in most cases at least.

APPARATUS AND REAGENTS

The combustions were made in a 100-cm. silica tube, having an internal bore of 23 mm., and with one-half its length made of transparent silica so that the process of combustion and the manipulation of the boat were under observation at all times. A 3-unit electric furnace was used, and the combustion tube was charged as shown in Fig. 1.

CERIUM OXIDE ASBESTOS¹ AND PUMICE—The asbestos catalyst was prepared by suspending highly purified, medium fibered asbestos in a saturated solution of chemically pure cerium nitrate and evaporating practically to dryness on a boiling water bath. The asbestos was then heated in a glass tube in a stream of oxygen, the escaping vapors being absorbed in dilute alkali. The cerium dioxide pumice, 12 mesh, recommended by Fisher and Wright² as more desirable than asbestos because of the tendency of asbestos to crumble and "sag," was similarly prepared. Reimer³ also had previously called attention to certain difficulties due to the crumbling of the asbestos impregnated with the cerium dioxide. However, no such difficulty arose with the asbestos used in this work. On the other hand, it remained throughout long service in the very desirable granulated condition which it assumed in the process of preparation.

LEAD PEROXIDE—It is very important that strictly pure peroxide be used for absorbing the nitrogen products. Considerable trouble was experienced at the beginning with a supposedly high-grade reagent.⁴ Previous to using, the peroxide was digested three times with boiling water, filtered, washed, and dried on a Büchner funnel in an electric oven. In charging the tube alternate layers of peroxide and peroxide asbestos were lightly tamped into a fine copper gauze container. The peroxide asbestos was prepared by intimately mixing about equal volumes of the two substances.

PURIFYING APPARATUS—This consisted of two 8-in. Peligot tubes filled as indicated in Fig. 1. Obviously, a purifying train filled in this manner will serve for a large number of combustions. The use of the phosphoric anhydride as the dehydrating agent is unnecessary unless accurate determinations of hydrogen are wanted.

ABSORPTION APPARATUS—Accuracy and speed were the principal advantages gained in the absorption ap-

¹ *J. Am. Chem. Soc.*, **40** (1918), 462.

² *Ibid.*, **40** (1918), 869.

³ *Ibid.*, **37** (1915), 1637.

⁴ The author is greatly indebted to Dr. W. D. Collins, U. S. Bureau of Chemistry, for furnishing him with a satisfactory peroxide manufactured by E. R. Squibb and Sons. The Bureau's analysis of Squibb's reagent gave 0.15 per cent soluble matter and 0.60 per cent sulfate.

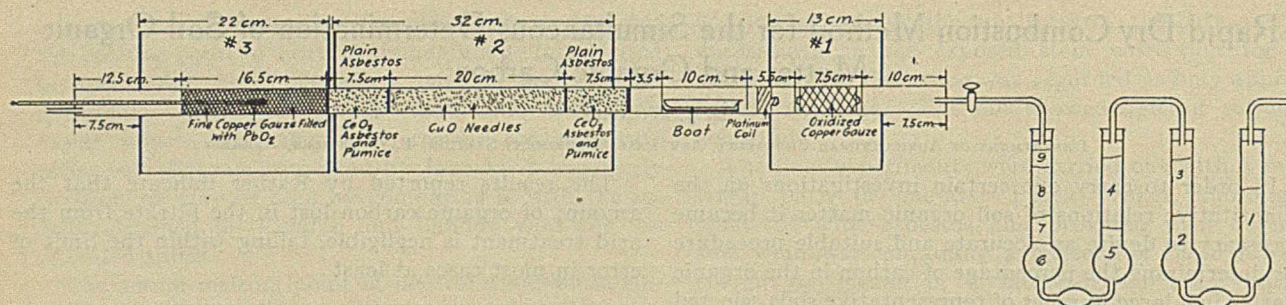


FIG. 1—CONTENTS OF TUBES BY SECTIONS

- 1—Calcium chloride
2—12-mesh soda lime
3—30-mesh soda lime

- 4—30-mesh soda lime
5—60-mesh soda lime
6—Calcium chloride

- 7—Short fibered asbestos
8—Phosphorus pentoxide
9—Asbestos

paratus, shown in Fig. 2, which also illustrates the manner of filling the apparatus. In the case of soils one filling of the absorption bulb served for more than several hundred determinations. The 30- and 60-mesh soda lime carrying 5 to 10 per cent moisture gave very efficient absorption. Nesbitt absorption bulbs, similarly filled, were also successfully used.

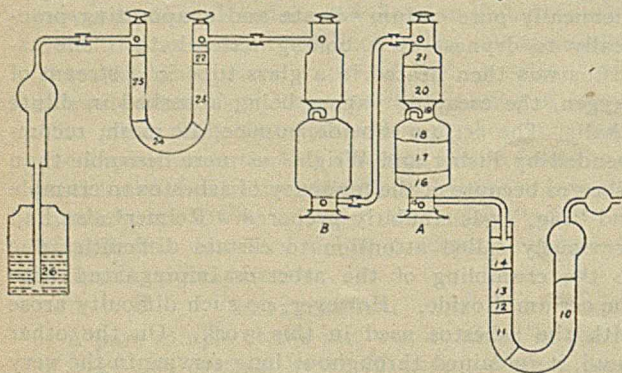


FIG. 2—CONTENTS OF TUBES BY SECTIONS

- 10—12-mesh pumice moistened with H_2SO_4
11—Glass wool
12—Asbestos
13—Phosphorus pentoxide
14—Glass wool
15—Asbestos
16—30-mesh soda lime
17—60-mesh soda lime
18—30-mesh soda lime
19—Asbestos
20—Phosphorus pentoxide
21—Asbestos
22—Asbestos
23—Phosphorus pentoxide
24—Glass wool
25—Calcium chloride
26—Palladium chloride solution

Tubes A and B are filled alike

PALLADIUM CHLORIDE SOLUTION—Palladium chloride solution,¹ prepared by adding 1 cc. of a 5 per cent solution to 200 cc. of distilled water, was used to detect any carbon monoxide resulting from imperfect combustion. No difficulty at all was experienced in this respect.

FILTERING—Filtration through the boat was accomplished quite satisfactorily by placing a rectangular piece of rubber, with a hole of the proper size and shape cut in its center, over the top of the funnel (Fig. 3), and then fastening the boat near each end on to the funnel by ordinary rubber bands, which were made sufficiently tight to secure good suction. The rectangular piece of rubber was cut from the inner tube of a motorcycle.

ASBESTOS—Baker's washed in acid and ignited, medium fibered asbestos was further purified by treating,

¹ Fisher, "Laboratory Manual of Organic Chemistry," 1920, 245. Wiley and Sons, Inc.

first, for several days with dilute hydrochloric acid, washing, and then treating in a similar way with dilute nitric acid. The asbestos was washed free of nitric acid with hot water and ignited to constant weight at high temperature in a muffle furnace.

WEIGHING SOIL SAMPLES

After drying in the electric oven for 16 hrs. at 99° C., the combustion boat containing the sample was cooled in a desiccator over phosphorus pentoxide and weighed with counterpoise in a "piggie" weighing tube, having a ground glass stopper. Since the samples of soil are very hygroscopic it is necessary to be exceedingly careful at this point. All weighings were made on a high-grade balance sensitive to 0.05 mg. and with a very high-class set of weights certified by the U. S. Bureau of Standards.

RUNNING THE COMBUSTION

The time required to begin and complete a combustion, including the initial and final weighings, averaged from 35 to 40 min. The time required to burn the sample and sweep out the tube varied from 13 to 20 min., depending on the percentage of organic matter present in the soil. All the combustions were made in a rapid current of air. The bubbling was several times faster than could be counted. The use of air appeared to remove certain difficulties in weighing the absorption bulbs shortly after completing the determination.

The boat containing the sample was carried in and out of the combustion tube on a platinum foil skid to prevent its gathering any of the loose copper oxide always present in the tube from the oxidized spiral. The sample was introduced into the tube and Units 1 and 2 were brought to bright redness before starting the combustion. The sample was burned by gradually bringing Unit 1 over the entire boat. From 5 to 9

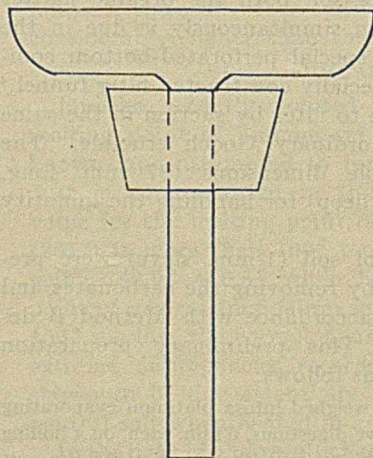


FIG. 3—FILTER FUNNEL FOR COMBUSTION BOAT

min. were required to burn the sample, and 8 to 11 min. more were used to sweep out the tube, during which time the two hot units cooled sufficiently to introduce another sample. The temperature of Unit 3, used for heating the lead peroxide, was kept between 300° and 320° C. by means of a long stem thermometer with its bulb placed in the center of the peroxide charge. Much above 320° C. decomposition of the absorption products formed with the nitrogen compounds took place. The absorption bulbs were always handled in duplicate under the same conditions to facilitate weighing. They were protected from the furnace heat by a thick shield of asbestos. The absorption of the carbon dioxide from the soil combustions never produced any perceptible change in the temperature of the bulb taking it up. Upon detaching the bulbs for weighing they were very carefully wiped with lens cloth and weighed after standing a very few minutes or just before their use another time. Two sets of bulbs were kept in use.

DATA

The data presented herewith are quite typical of the several hundred combustions made without recharging the combustion tube or either the purifying or absorption trains. The determinations are given in

duplicate. The furnace was checked on a standard sample of sucrose received from the Bureau of Standards, with the following results in percentages of carbon, —42.06, 42.13, 41.99. Theoretical = 42.08.

Registration Number	Type of Soil	Depth of Sample Inches	Per cent Organic Matter			Per cent Carbon in Organic Matter		
			(1)	(2)	Av.	(1)	(2)	Av.
2654	Lamour silty clay loam	0-20	6.17	6.20	6.18	54.94	54.63	54.78
2655	Subsoil to 2654	20-36	1.13	1.15	1.14	46.44	46.95	46.64
2656	Webster silty clay loam	0-15	3.66	3.59	3.62	50.59	50.66	50.62
2657	Subsoil to 2656	15-36	1.23	1.21	1.22	47.22	47.10	47.16
2658	Wabash silty loam	0-20	6.18	6.18	6.18	55.46	55.43	55.44
2659	Subsoil to 2658	20-36	2.17	2.21	2.19	56.67	56.44	56.55
2672	Decatur silty loam	0-10	1.72	1.64	1.68	47.08	47.05	47.07
2673	Subsurface soil to 2672	10-20	0.076	0.074	0.075	26.55	26.90	26.72
2674	Subsoil to 2672	20-36	0.044	0.048	0.046	22.93	22.72	22.82
2675	Grundy silty loam	0-12	2.71	2.70	2.70	52.91	52.96	52.93
2676	Subsurface soil to 2675	12-18	1.01	1.05	1.03	42.12	42.07	42.09
2677	Subsoil to 2675	18-36	0.076	0.087	0.081	27.98	28.21	28.08
2792	Diablo clay	0-24	1.38	1.39	1.38	49.00	49.05	49.02
2793	Subsoil to 2792	24-72	1.07	1.09	1.08	42.56	42.28	42.42

SUMMARY

The simultaneous determination of the organic matter and the organic carbon by the above method effects a saving in time of approximately 60 per cent.

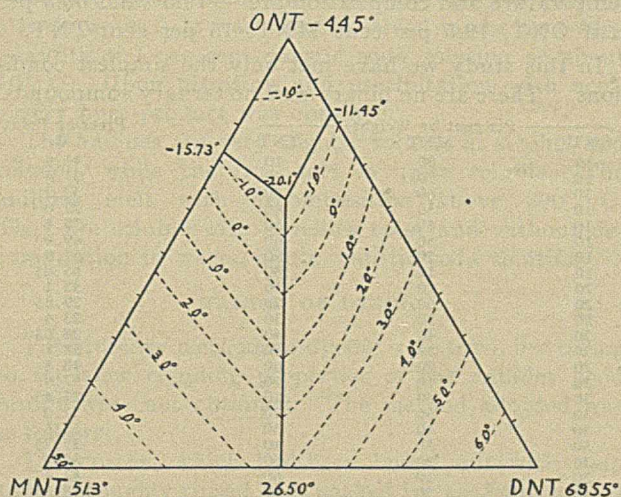
It is believed that the data secured on the many soils which have been investigated are more accurate than could have been obtained by any previously described method, and that the magnitude of error is reduced to a minimum.

Studies on the Nitrotoluenes. VI—The Three-Component System: *o*-Nitrotoluene, *p*-Nitrotoluene, 1,2,4-Dinitrotoluene^{1,2}

By James M. Bell and Edward B. Cordon

UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.

In a previous paper of this series by Bell and Herty,³ the cooling-curve method of obtaining the freezing points of various three-component mixtures has been described. The present paper contains the results



obtained by the same method for another three-component system of the nitrotoluenes. We shall not repeat the details of the method or the methods of preparation of the pure components, but shall

refer to some of the features of this system. A foregoing paper¹ has shown the existence of two forms of ONT, and therefore there should be two charts for this present study: One where the component, ONT, is in its stable form, and one where it is in its metastable form. These two charts would be identical except in the portion of the diagram where ONT is the solid phase. Reference to the foregoing paper

Per cent by Weight			Freezing Point °C.
DNT	MNT	ONT	
80	10	10	56.01
70	10	20	47.85
70	20	10	47.75
60	10	30	38.82
60	20	20	38.66
60	30	10	38.01
50	10	40	27.52
50	20	30	26.98
50	30	20	26.47
50	40	10	27.47
40	10	50	12.08
40	20	40	10.55
40	30	30	9.84
40	40	20	13.84
40	50	10	21.82
30	10	60	2.45
30	20	50	-4.19
30	30	40	-9.50
30	40	30	-9.74
30	50	20	20.15
30	60	10	29.39
20	10	70	-13.20
20	20	60	-3.89
20	30	50	8.48
20	40	40	19.10
20	50	30	27.83
20	60	20	35.69
20	70	10	11.82
10	10	80	-15.65
10	20	70	-5.95
10	30	60	7.64
10	40	50	17.55
10	50	40	27.08
10	60	30	34.25
10	70	20	41.32
10	80	10	

¹ Received December 21, 1920.
² This paper is the sixth of a series dealing with the freezing points and thermal properties of the nitrotoluenes, the investigation having been undertaken at the request of the Division of Chemistry and Chemical Technology of the National Research Council.
³ THIS JOURNAL, 11 (1919), 1128.

shows why we were unable to obtain points where stable ONT was the solid phase, for neither binary eutectic, ONT-MNT or ONT-DNT, was found in the presence of metastable ONT. All the points in the diagram in the top field represent liquids saturated with respect to stable ONT.

Again we have observed the tendency for great supercooling with respect to DNT, and therefore we have been compelled to seed with crystals of that substance. The approach to equilibrium after seeding is also somewhat slow, and rather long extrapolations have been necessary.

The position of the boundary curves has been established by the method of the paper already cited. The freezing points of mixtures with a constant percentage of one component have been plotted. The points lie on two curves which intersect at the boundary curve, and the composition and temperature given by the plot establish one point on the boundary curve. The complete boundary curve may be obtained by finding a number of such points. The

intersection of the three boundary curves fixes the composition of the ternary eutectic, found in this case to be 62 per cent ONT, 19 per cent MNT, and 19 per cent DNT.

For most of the low-temperature work we used a bath of ice and salt, but for temperatures in the neighborhood of the ternary eutectic a lower temperature was necessary. For this purpose we used a bath of mixed carbon tetrachloride and gasoline in which was a coil of metal tubing connected with a tank of liquid ammonia, tilted so as to deliver the liquid at the control valve. The evaporation of the liquid into the metal coil lowered the temperature sufficiently to obtain cooling curves for the lowest freezing mixtures.

The ternary eutectic temperature was reached by first obtaining the binary eutectic mixture, ONT-MNT, and by adding DNT in small quantities. Each addition lowered the temperature until no more DNT would pass into the melt. When the liquid is saturated with DNT also, the ternary eutectic has been reached, in this case at -20.1° .

Studies on the Nitrotoluenes. VII—The Three-Component System: *p*-Nitrotoluene, *o*-Nitrotoluene, 1,2,4,6-Trinitrotoluene^{1,2}

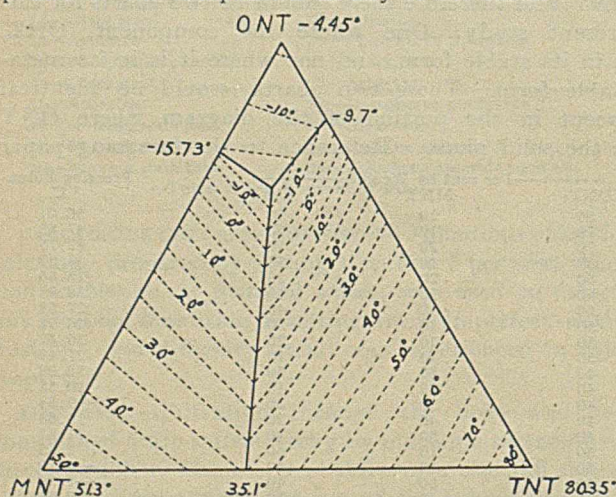
By James M. Bell and Fletcher H. Spry

UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.

All the binary systems of the components: *p*-nitrotoluene (MNT), *o*-nitrotoluene (ONT), and 1,2,4,6-trinitrotoluene (TNT) have already been described in previous articles of this series.³ In each case the freezing-point curves consist of two lines intersecting in a eutectic point. There is no compound of the components in any of the cases.

these crystals being necessary. The accompanying table comprises only data for three-component mixtures, the temperatures along the sides of the triangle having already been recorded in the articles referred to above. The positions of the boundary curves and of the eutectic point were determined by the method described by Bell and Cordon.¹ The diagram shows the boundary curves with 5° isothermals. The eutectic temperature and composition are -19.5° and 65.5 per cent ONT, 19.5 per cent MNT, 15 per cent TNT.

In this study we have met only the simplest conditions. There are no binary and no ternary compounds.



In the study of the three-component system we have followed the methods already outlined in these articles. The freezing points where ONT is the solid phase refer to the stable form (β -ONT), seeding with

¹ Received December 21, 1920.

² This paper is the seventh of a series dealing with the freezing points and thermal properties of the nitrotoluenes, the investigation having been undertaken at the request of the Division of Chemistry and Chemical Technology of the National Research Council.

³ MNT-ONT and TNT-ONT, Bell, Cordon, Spry and White, *THIS JOURNAL*, 13 (1921), 59; MNT-TNT, Bell and Herty, *Ibid.*, 11 (1919), 1124.

Per cent by Weight			Freezing Point ° C.
ONT	MNT	TNT	
10	80	10	41.9
10	70	20	37.4
10	60	30	32.2
10	50	40	29.0
10	40	50	38.4
10	30	60	49.4
10	20	70	57.9
10	10	80	65.65
20	70	10	35.1
20	60	20	29.85
20	50	30	23.4
20	40	40	28.64
20	30	50	38.7
20	20	60	48.4
20	10	70	57.9
30	60	10	27.43
30	50	20	21.0
30	40	30	13.8
30	30	40	27.23
30	20	50	38.8
30	10	60	47.4
40	50	10	18.85
40	40	20	10.85
40	30	30	12.35
40	20	40	26.63
40	10	50	37.6
50	40	10	7.5
50	30	20	-3.8
50	20	30	9.95
50	10	40	25.47
60	30	10	-18.5
60	20	20	-12.0
60	10	30	8.6
70	20	10	-16.3
70	10	20	-10.5
80	10	10	-11.9

The Anilides of β -Oxynaphthoic Acid¹

By E. R. Brunskill

CINCINNATI CHEMICAL WORKS, NORWOOD, OHIO

The colors obtained by substituting β -oxynaphthoic acid for β -naphthol in the ice process are brighter and are of a somewhat greater range in shade. They do not have the brownish appearance which β -naphthol colors sometimes have, and the solutions can be kept longer and with more ease than is the case with β -naphthol. The β -oxynaphthoic acid colors, however, have the very serious fault of washing out easily, and are not fast to rubbing. In order to overcome these serious defects the carboxy-group has been covered by substituted amines, the principal one of which is the anilide, known also as Naphthol AS.

A great number of the anilides of β -oxynaphthoic acid are described in the patent literature, but for the comparison to be made here only the anilide, the p -toluidide, and the p -chloroanilide are considered.

METHOD OF PREPARATION

They were made by a process similar to those described in the various patents.

One mole (in grams) of β -oxynaphthoic acid, one mole of amine, and 1400 cc. of toluene were heated to gentle boiling under a reflux condenser. Then, with stirring, the theoretical quantity of phosphorus trichloride was slowly dropped in. The hydrochloric acid gas evolved was absorbed over water, and the reaction was ended when no more gas was evolved. The time required was from 2 to 4 hrs. The mixture was poured into water and the toluene drawn off. The water suspension of the anilide was made slightly alkaline with soda ash, in which the anilide is insoluble. The solution, containing the uncombined β -oxynaphthoic acid, was filtered, and the precipitate washed with a little water. It was then dissolved in the necessary quantity of 1 per cent caustic soda solution at about 50° C. Upon filtration and precipitation with acid, a very pure product was obtained.

The anilides are very slightly soluble in alcohol and toluene, while the free acid is quite soluble. The anilides melt with decomposition above 200° C. They are soluble with a yellow color and without decomposition in warm, dilute, caustic soda solution.

METHOD OF DYEING

The ordinary methods of dyeing were tried, but owing to the slow coupling properties of the anilides good results were not obtained. The method adopted was as follows:

The cotton, which had been boiled out with soap and thoroughly rinsed, was soaked for an hour in a 2 per cent solution of the anilide in the theoretical amount of caustic soda. In the meantime the diazo solutions were prepared in the usual manner and made up to a concentration of 0.1 mole in 500 cc. An ice-cold saturated salt solution was treated with enough soda ash to make a 3 per cent solution, and fil-

tered to remove the precipitated CaCO_3 , BaCO_3 , and MgCO_3 .

To dye a 10-g. skein, 300 cc. of the cold salt solution were measured into a liter beaker. The thoroughly wrung skein of treated cotton was immersed in the salt solution, and immediately 80 cc. of the diazo solution were added, with constant turning of the cotton. The cotton was turned for about an hour, then rinsed first in cold water, then in hot soap solution, and finally in warm water. In the developing bath a test should show a slight excess of soda ash and diazo compound at the finish. If not, more of the one which was lacking should be added for another dyeing, as the best dyeings were obtained only by adding all the materials at once.

Dyeings were made using the following substances as naphthols: β -oxynaphthoic acid, the anilide, the toluidide, and the p -chloroanilide. Each naphthol was coupled with aniline, p -nitroaniline, p -chloroaniline- o -sulfonic acid, p -toluidine, m -nitro- p -toluidine, and o -chloro- p -toluidine sulfonic acid.

All the colors made from β -oxynaphthoic acid washed out and were not fast to rubbing, especially those made from the sulfonated amines. Moreover, the colors were not as bright as those made from the anilides. The anilides gave colors which were fairly fast to washing and rubbing, except in the case of the sulfonated amines.

In order to make the colors from the latter faster to washing they were treated as follows:

The damp rinsed dyeings were dipped into a 3 per cent solution of calcium chloride and allowed to remain with turning for a half hour at 50° C. They were then rinsed and dried. This treatment made the colors fast to washing and rubbing, with but very little change in shade.

All the β -oxynaphthoic acid colors were also treated with calcium chloride, which made them much faster to washing, notably in the case of p -chloroaniline- o -sulfonic acid.

One might expect to obtain a difference in color between the three anilides, and as far as these dyeings show there are some differences, but, before one could definitely say just what effect a substituent in the amine of the amide has upon the color, a larger number of anilides must be studied.

It appears, however, that the p -chloroanilide, and the p -toluidide give brighter shades than the anilide, and that the p -chloroanilide gives a slightly brighter shade than the p -toluidide, except in the case where there is a nitro group in the diazotized amine, in which case the p -toluidide gives the brightest colors.

The effect of the nitro group can also be observed by comparing the colors from p -nitroaniline and m -nitro- p -toluidine, those from the latter being in every case the brightest, so that it seems that a nitro group must be balanced with a methyl group in order to obtain the best results.

¹ Presented before the Division of Dye Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

The Non-Biological Oxidation of Elementary Sulfur in Quartz Media¹

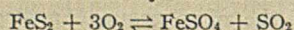
[PRELIMINARY REPORT]

By W. H. MacIntire, F. J. Gray and W. M. Shaw

UNIVERSITY OF TENNESSEE, AGRICULTURAL EXPERIMENT STATION, KNOXVILLE, TENNESSEE

The conversion of native organic sulfur into sulfates in soils is generally considered to be an almost exclusively biological process. The oxidation of added elementary sulfur is likewise usually attributed to the action of bacteria. The native organic sulfur phase of sulfate generation, as influenced by calcium and magnesium materials in varying amounts, has been under investigation at the University of Tennessee Agricultural Experiment Station since July 1914. At that time, forty-six lysimeters were filled with Cumberland loam, twenty-three tanks having soil alone, and twenty-three having surface soil above a 1-ft. layer of clay subsoil. Each annual aggregate of sulfate leachings has been determined quantitatively. Divergent effects of calcium and magnesium compounds upon the sulfate outgo during the first two years were reported upon in a preliminary paper by the writer and associates.² The supplementary study of sulfur additions to a Cherokee sandy loam was begun in August 1917. Fifteen tanks received sulfur additions. Each 5-tank group received one of the three forms of sulfur: namely, iron sulfate, iron pyrite, and flowers of sulfur, each in an amount equivalent to 1000 lbs. of sulfur per 2,000,000 lbs. of soil. The question of the influence of lime and magnesia upon added sulfur was also included in the supplementary study. In this second installation, comprising twenty-two lysimeters, the loss of sulfur, as leached sulfates, was determined for each tank periodically, as necessitated by the unsupplemented rainfall. The data secured demonstrated that the flowers of sulfur and iron pyrite were both converted into sulfates with distinct rapidity.

It was at first assumed that the oxidation of both the elementary sulfur and that of the pyrites was induced in the main, if not solely, by organisms. However, some doubt concerning this assumption was introduced about 2 yrs. after the inauguration of the experiment, when it was observed that a strong odor of sulfur dioxide was given off from the reserve sample of iron pyrites, which had been kept in the dark in an 8-oz. glass bottle, tightly stoppered with an ordinary No. 6 cork stopper. A 10-g. charge of the pyrites was found to yield soluble sulfate of iron, equivalent to a determined weight of 0.4172 g. of BaSO₄, as an average of seven determinations. The same observation has been reported by Allen and Johnston³ in 1910. These workers further reported that an increase of 100 per cent of sulfate of iron was caused by grinding for a period of 1 hr. They accounted for the reaction by means of the equation:



Contact of moist pulverized metallic iron and flowers of sulfur was found to produce iron sulfide,

a reaction which was also found to be recorded.¹ These observations suggested the possibility that the applied elementary sulfur might combine to a certain extent with the iron of the soil, forming compounds which, in turn, would undergo oxidation to sulfates. It even seemed plausible to assume that the presence of iron might be essential to the extensive conversion of elementary sulfur into sulfates.

These observations led to a laboratory study of the two major queries:

1—What function, if any, does metallic iron, and what function does iron oxide, or oxides, have upon the conversion of elementary sulfur to sulfates in soils?

2—Will the effects possibly induced by iron, or its oxides, be independent of biological activation?

EXPERIMENTAL METHOD

It was planned to study the oxidation of elementary sulfur in the absence of appreciable quantities of iron, under aerobic and anaerobic conditions, with the unaltered medium, the sterilized medium, and the medium plus inoculation. The purest obtainable quartz was used as the medium for sulfur additions. An unsuccessful attempt was made to secure an iron-free quartz. The finely ground New England quartzite used ran 99.28 per cent SiO₂, 0.34 per cent Fe₂O₃, and 0.0096 per cent S. The purest hydrogen-precipitated iron obtainable (0.0475 per cent sulfur) was used as one source of iron. The other iron compound used was limonite, analyzing 39.50 per cent iron and 0.013 per cent soluble sulfate sulfur.

Five hundred-cc. Pyrex flasks were used as containers for the treated media. The very finely ground, unleached quartz was used in the constant amount of 250 g., with 14 per cent distilled water additions for moisture. Each medium was kept in the dark for a period of 60 days after treatment. In addition to the constant amount of quartz the following single or combined constants were used: 0.1251 g. of sulfur; 10.0806 g. of metallic iron; 25.3164 g. of limonite; 0.5076 g. of C. P. precipitated calcium carbonate; 0.5000 g. of C. P. precipitated magnesium carbonate; 0.5181 g. of 100-mesh limestone; and 0.5449 g. of 100-mesh dolomite. The calcium and magnesium materials were chemically equivalent.

The biological conditions maintained in the original quartz-medium experiments were:

- 1—Unaltered quartz.
- 2—Quartz sterilized by heat.
- 3—Inoculation by soil infusion "A."
- 4—Inoculation by soil infusion "B."

These four conditions were maintained under aerobic and anaerobic conditions. The aerobic flasks, both sterile and nonsterile, were stoppered with cotton plugs. The anaerobic atmosphere was produced by a 6-hr. passage of purified carbon dioxide.

¹ S. P. Sadtler and V. Coblenz, "Pharmaceutical and Medicinal Chemistry," 3rd Ed., Vol. I, 574.

¹ Received December 11, 1920.

² W. H. MacIntire, L. G. Willis and W. A. Holding, *Soil Sci.*, 4 (1917), 231.

³ "The Exact Determination of Sulfur in Pyrite and Marcasite," *This Journal*, 2 (1910), 196.

TABLE I—SUMMARY SHOWING SOLUBLE SULFATES ENGENDERED FROM CONTACT OF FLOWERS OF SULFUR WITH POWDERED QUARTZ AND VARIOUS ADDITIONS
Sulfate increases expressed as lbs. of S per 2,000,000 lbs. of medium. Uniform rate of sulfur additions, equivalent to 1000 lbs. per 2,000,000 lbs. of medium. Total of 118 distilled water extractions after 60 days of contact

Materials Added to 250 G. of Quartz	Access to Atmosphere through Cotton Plugs—					Sealed Atmosphere of CO ₂				
	Unaltered Quartz	Sterilized Quartz	Thrice Infusion Soil A	Infusion Soil B	Average of Treatment	Unaltered Quartz	Sterilized Quartz	Thrice Infusion Soil A	Infusion Soil B	Average of Treatment
Sulfur only.....	213.1	198.1	241.0	237.7	222.5	243.2	138.3	40.7	167.0	147.3
Sulfur and CaCO ₃	623.0	210.9	423.9	505.5	440.8	352.4	...	154.1	239.3	248.6
Sulfur and limestone.....	516.4	192.9	404.9	321.9	359.0	412.0	...	199.5	228.4	280.0
Sulfur and MgCO ₃	774.3	142.6	245.4	266.1	357.1	34.4	50.3	143.7	65.0	73.4
Sulfur and dolomite.....	598.4	134.4	410.4	482.6	406.5	379.8	146.4	225.7	182.0	233.5
Average for carbonate group.....	628.0	170.2	371.2	394.0	390.9	294.7	98.4	180.8	178.7	208.9
Sulfur and Fe.....	89.0	86.9	68.3	63.9	77.0	-39.9	-37.7	-18.0	-23.5	-29.8
Sulfur, CaCO ₃ , and Fe.....	172.1	123.0	84.7	70.5	112.6	-27.9	-32.2	-19.1	-8.2	-21.9
Sulfur, limestone, and Fe.....	167.8	170.3	78.1	129.5	136.4	-39.9	-37.2	-36.6	-22.4	-34.0
Sulfur, MgCO ₃ , and Fe.....	154.1	58.5	73.8	91.8	94.6	-42.1	-26.8	-20.2	-16.9	-26.5
Sulfur, dolomite, and Fe.....	169.9	112.1	127.9	104.9	128.7	-29.0	-50.8	-48.6	-27.8	-39.1
Average for iron group.....	150.6	110.2	86.6	92.1	109.5	-35.8	-36.9	-28.5	-19.8	-30.3
Sulfur and limonite.....	490.7	222.9	657.9	453.6	456.0	280.3	312.6	149.2	134.9	219.3
Sulfur, CaCO ₃ , and limonite.....	560.1	316.8	539.9	624.1	510.2	383.6	361.7	25.1	110.4	220.2
Sulfur, limestone, and limonite.....	495.1	231.7	594.6	592.4	478.5	334.4	403.2	146.5	166.7	262.7
Sulfur, MgCO ₃ , and limonite.....	680.9	270.0	341.6	356.9	412.4	185.2	145.3	154.6	139.9	156.3
Sulfur, dolomite, and limonite.....	579.2	186.9	673.8	636.1	519.0	343.7	376.0	154.6	143.1	254.4
Average for limonite group.....	561.2	245.7	561.6	532.6	475.2	305.4	319.8	126.0	139.0	224.6
Grand average—showing effect of chemical treatment given quartz.....	418.9	177.2	331.1	329.2	314.1	184.7 277.0 ¹	132.2 218.6 ¹	92.9 139.4 ¹	105.1 157.7 ¹	129.6 194.4 ¹

¹ Not including the less-than-check iron group.

An additional series containing purified hydrogen was also subjected to experimental treatment, but this series is not yet ready for report.

The sterilization was effected by three successive daily heatings in the autoclave, without contact of quartz, and the separately sterilized materials used in the several treatments. The sterile added materials were mixed throughout the dry sterile quartz immediately before the addition of the constant moisture content, every care being taken to insure continued sterility. All of the stoppered flasks were put away in the dark, in a room relatively free from fumes, for a period of 60 days. At the end of the 60-day period the contents of the flasks were extracted by addition of cold distilled water to near-complete volume. After 4 hrs.' shaking and standing over night, the extracts were filtered with double filters through Büchner funnels. Each residue was then thoroughly mixed and returned to its original flask for an additional period of contact of 40 days, after which the filtration was repeated. The filtrates were analyzed for sulfides, and, if necessary, sodium hydroxide was introduced. They were then acidified and evaporated to dryness, in order to remove silica. The engendered sulfates, as well as the sulfates of all blanks, were determined gravimetrically. Tests were made to insure the fact that the precipitates were not barium fluoride. In addition to the eight series of fifteen flasks each, an additional set of twelve flasks was run simultaneously. Three flasks contained inoculated quartz and nitrate nitrogen to the extent of 10 mg. of nitrogen, one flask containing sodium nitrate, one calcium nitrate, and one magnesium nitrate. These three nitrate treatments were duplicated with an increase of nitrate nitrogen to a basis of 50 mg. The six flasks above described were then duplicated as to nitrogen treatment, but with the addition of 10.0806 g. of metallic iron to each flask.

The details of the scheme of treatment and the summary of available leaching data are set forth in Tables I and II. The calcium and magnesium materials were not added upon the assumption that they would react directly with the sulfur, but in order to pre-

vent the possible accumulation of free end-product acids. These data represent the summation of a number of tables secured from the analysis of leachings after the first period of 60 days and are corrected by subtraction of the soluble sulfates leached initially from the single or combined treatments, as determined upon the separate materials. Most of the sulfates leached from the second 40-day period have been determined and will be included in the more detailed report to be published at an early date. The data are given in pounds of sulfate sulfur, per 2,000,000 lbs. of quartz, recovered from the added flowers of sulfur, which was applied in amounts equivalent to 1000 lbs. of sulfur per 2,000,000 lbs. of quartz.

Some further studies involving the use of water-leached and acid-leached quartz media are also being used for further study of the transformations following additions of elementary sulfur. The influence of a combination of metallic iron and limonite is also being studied with regard to antagonism. It has been found that such a combination evolves considerable amounts of heat. An effort is also being made to determine whether or not the generation of sulfur under the conditions maintained would have any effect upon the solubility of simultaneously added and intimately mixed rock phosphate.

DISCUSSION OF RESULTS

The data of Table I show a number of consistent and striking relationships. In the case of the flasks having limited access to air, the unaltered and untreated quartz shows a gain in sulfate, as do also the portions sterilized and inoculated. The first group of calcium and magnesium supplementary materials, to be considered, in a sense, as checks, shows a distinct increase in sulfates above the gain shown by the quartz and sulfur alone, induced directly or indirectly, in the three conditions other than sterilized. In the metallic iron group the consistent depressive action of iron alone is strikingly demonstrated; while the oxidizing tendency of the supplementary carbonate materials is shown by the excess of sulfates where these materials are included, as contrasted with the iron alone.

In the third, or limonite, group there is demonstrated an acceleration in sulfur oxidation, particularly as contrasted with the depressive tendency exhibited by the metallic iron group. This holds true for limonite alone and limonite as supplemented by the carbonate materials. On comparing the four carbonate-limonite additions with the four carbonate-only treatments, it would seem that both materials are, in part, responsible for the general tendency toward increase when the combined treatments are made. Although the heat-sterilized flasks yielded less sulfur than did the unaltered quartz, this fact could not be considered as positively indicating eradication of biological agencies by heat. It is possible that the repeated heating may have depressed the activation of the materials able to induce chemical oxidation; for it will be noted that the two inoculations did not increase the sulfate yield above that of the original unaltered quartz. Then, too, such repeated heatings might be considered as dissipating a part, or the whole, of any oxidizing atmosphere which may be condensed upon the surface of the quartz particles.

Considering the anaërobic carbon dioxide series, we find certain striking results. The elementary sulfur in the quartz-sulfur flasks appears to have utilized oxygen from either the carbon dioxide of the atmosphere, water, or silica. It appears hardly conceivable that silica could be considered as a source of oxygen for the oxidation phenomenon. However, in the case of the carbonate materials, the combined carbon dioxide may be considered as possibly having either a direct or indirect influence upon the acquisition of oxygen by the elementary sulfur. But, since the distilled water used to maintain a uniform moisture contact was freed of gases by boiling, the oxygen could have come from no other sources, unless it be assumed that appreciable quantities of oxygen or air were condensed upon the surface of the quartz particles. This hypothesis would necessarily be predicted upon the assumption that such a condensed gas is tenaciously held by physical attraction, but is, at the same time, extensively available chemically for the oxidation of the added materials under conditions of intimate moist contact. None of the treatments leached up to this point have been tested for an occurrence of free hydrogen, but several have been tested for carbon monoxide. In one case, a quantitative determination gave 280 mg. of carbon monoxide in the absence of limonite.

It appears that the magnesium carbonate has a distinct depressive tendency upon the oxidation of sulfur in the presence of an atmosphere of carbon dioxide. The cause of this particular phenomenon will not be considered at this time except to point to the ready solubility of $MgCO_3$ in carbonated water. It will be noticed, moreover, that this distinctive depressive action of magnesium carbonate is not obtained in a case of the aërobic group.

A study of the metallic iron group shows that, in every case of the twenty treatments, we find a posi-

tive depression to the extent of being below the actual determined blank in each instance. The depression induced by iron was decidedly accentuated in the anaërobic atmosphere, as compared with the aërial atmosphere, no one treatment of which gave a recovery less than the corresponding blanks. It would seem that the oxygen available, in whatever form, is more readily attached to the metallic iron than to the elementary sulfur. The occurrence of ferric hydrated oxide is readily noted when the contents of the flasks are subjected to extraction and leaching.

Again, in noting the sulfate recovered from the limonite group, we find that the limonite alone, and when supplemented, is responsible for acceleration in the formation of leachable sulfates. In this group, as in the corresponding group under aërobic conditions, it is difficult to differentiate quantitatively between the results induced by the limonite and those induced by the carbonate, when the combination treatments were made. It is apparent, however, that both the mineral carbonates and calcium carbonate have the accelerative tendency exhibited by limonite in the generation of sulfates.

Here, again, we note the same retarding tendency exhibited by the magnesium carbonate in the presence of carbonated water that was manifested in the case of the magnesium carbonate treatment alone, under the anaërobic condition. It is rather strikingly demonstrated that the presence of limonite tends to restrict, or offset, the depressive influence exhibited by the precipitated magnesium carbonate wherein contact with carbon dioxide was maintained, which was so distinctly recorded in the first group of calcium and magnesium materials alone.

TABLE II—SHOWING INFLUENCE OF IRON AND OF NITRATE NITROGEN UPON OXIDATION OF ELEMENTARY SULFUR
Added at rate of 1000 lbs. per 2,000,000 lbs. of medium. Soil infusion; CO_2 atmosphere; 60-day and 40-day periods of contact

Materials Added to 250 G. of Quartz	Sulfate Sulfur Leached, Lbs. per 2,000,000 Lbs. of Medium after 60 Days	Sulfate Sulfur Leached after Removal of Nitrate Nitro- gen, Effected by First Extrac- tion—40-Day Period of Contact
Sulfur only.....	40.7	188.1
Sulfur and 10 mg. N as $NaNO_3$	173.7	218.0
Sulfur and 10 mg. N as $Ca(NO_3)_2$	132.8	167.2
Sulfur and 10 mg. N as $Mg(NO_3)_2$	253.0	222.4
Group average for 10 mg. N.....	186.5	202.5
Sulfur and 50 mg. N as $NaNO_3$	12.5	302.2
Sulfur and 50 mg. N as $Ca(NO_3)_2$	3.2	236.0
Sulfur and 50 mg. N as $Mg(NO_3)_2$	4.4	195.3
Group average for 50 mg. N.....	6.7	244.5
Sulfur, 10 mg. N as $NaNO_3$ and Fe.....	-38.8	+8.7
Sulfur, 10 mg. N as $Ca(NO_3)_2$ and Fe.....	-35.3	+16.4
Sulfur, 10 mg. N as $Mg(NO_3)_2$ and Fe.....	-33.3	+19.1
Group average for 10 mg. N and Fe.....	-35.8	+14.7
Sulfur, 50 mg. N as $NaNO_3$ and Fe.....	-12.5	+13.6
Sulfur, 50 mg. N as $Ca(NO_3)_2$ and Fe.....	-30.0	+15.3
Sulfur, 50 mg. N as $Mg(NO_3)_2$ and Fe.....	-34.4	+13.6
Group average for 50 mg. N and Fe.....	-25.6	+14.2

The contents of Table II are from the simultaneous supplementary experiment. In this particular instance, the three forms of nitrate nitrogen, such as might be found in a normal soil, were introduced along with an infusion from a soil of known sulfifying capacity. It is consistently shown that the presence of added nitrate has an effect upon the generation of sulfate. The greater depression induced by the larger amounts

of the oxygen-carrying salts indicates that the concentration of salts in the moisture of the medium is a potent factor in the speed, if not ultimate extent, of the sulfate formation. It is quite possible that this factor of salt concentration in the moisture of the medium may account for the depressive action exhibited by magnesium carbonate in the carbon dioxide atmosphere, as compared with the anaërobic condition, since magnesium carbonate is exceedingly soluble in carbonated water.

The data relative to the amounts of sulfates leached after the second exposure of 40 days, subsequent to the removal of both added nitrate and generated sulfates, confirmed the point indicated by the results from the first contact. Here, again, we find the depressive tendency of metallic iron prevailing, though nitrates were present. It is a rather striking fact that these six determinations added to the corresponding data of Table I give us twenty-six determinations of remarkable consistency relative to the influence of metallic iron upon the formation of sulfates. In every one of the twenty-six treatments (excepting the one instance of an increase of but 1.1 lbs.), involving additions of metallic iron, the recovery is below the amount actually determined as being present initially in the added materials, singly and in combination. It would appear, also, that not only does the metallic iron preempt the available oxygen, but it also effects a reduction of the sulfates originally present as impurities in the several materials.

The problem of the function of surface in effecting oxidation is one which is also being considered. The presence of the quartz medium exerts a certain definite increase in the end-products, within a definite time, over the amounts found where the reaction takes place in the absence of silica. As an example, a mixture of quartz, sulfur, and limonite, boiled gently over night with distilled water, gave an increase amounting to 3.2 times that obtained when the sulfur and limonite were boiled together without quartz. It is hoped to remove part, or all, of any condensed atmosphere upon the quartz particles and then study the oxidation induced thereafter. The fact that we have secured the extensive oxidation of sulfur added to quartz in an atmosphere of hydrogen eliminates the assumption that the phenomenon is necessarily induced by the oxygen of the atmosphere, or that of the carbon dioxide gas.

It should be made plain that it is not our thesis to prove that sulfofying organisms are not responsible for transformation of sulfur into sulfates in the soil mass. This is particularly true with reference to native or added organic sulfur materials. Granting that the transformation of added elementary sulfur into sulfates may be, in part, a function of the biological content of the soil, nevertheless, the quartz-medium data presented seem to point very conclusively to the fact that added elementary sulfur may be also readily and extensively transformed into sulfates, by independent chemical action under aerobic and anaërobic, sterile and nonsterile conditions of

moist contact at normal temperature, when ferric oxides and alkali-earth carbonates are present.

A detailed report of these and other studies along the same lines will be offered shortly, together with some consideration of the chemical explanations to be advanced as accounting for the oxidation, with such suggestions as the work may carry relative to other oxidation reactions in the soil.

Annual Tables of Constants

Assembled and published by an International Commission acting under the authority of the International Union of Pure and Applied Chemistry.

COMMISSIONERS

CH. MARIE (France), General Sec'y	PAUL DUTOIT (Switzerland)
G. CARRARA (Italy)	ALFRED EGERTON (England)
ERNST COHEN (Holland)	E. W. WASHBURN (United States)

The publication of the "Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological," which was interrupted during the war, has now been resumed. Subscriptions to Volume IV, containing all numerical data published during the years 1913 to 1916, inclusive, will be received up to May 31 at the special reduced rates indicated below. The edition will be limited, and the price will be raised after May 31.

ADVANCED SUBSCRIPTION RATES FOR VOL. IV (Effective until June 1, 1921)

	—Part I Only—		—Parts I and II—	
	Bound	Unbound	Bound	Unbound
A. Regular.....	\$12.50	\$11.00	\$25.00	\$22.00
B. Special (To members of the American Chemical Society).....	9.50	8.00	19.00	16.00

Vol. IV is divided into two parts, Part I containing the constants from "Compressibility" to "Electricity" (see Table of Contents, Vol. III), and Part II the remaining constants. Part I will be delivered probably early in July and Part II some months later. Subscribers to both volumes will receive Part I on the July delivery.

Subscribers whose payments accompany their subscriptions will receive the volumes carriage free. To others delivery will be made by C. O. D. express.

Orders for Volumes I, II, and III will be received at \$7.20 each. Vol. I is, however, not sold separately, owing to the limited supply.

Volume V, covering the years 1917 to 1920, inclusive, is in preparation and will be ready for distribution late in 1922.

Orders from members of the SOCIETY should include the statement: "I hereby certify that I am a member of the AMERICAN CHEMICAL SOCIETY."

The British Dyestuffs Committee

In accordance with the provisions of the British Dyestuffs Act of 1920, the following committee has been appointed by the Board of Trade to advise with respect to the granting of licenses under the Act:

VERNON CLAY, Joint Managing Director, Robert Clay, Ltd.
GEORGE WELSH CURRIE
GEORGE DOUGLAS, Managing Director, Bradford Dyers' Association, Ltd.
E. V. EVANS, O.B.E., F.I.C., Treasurer, Society of Chemical Industry
MARTIN ONSLOW FORSTER, F.R.S., F.I.C., Director, Salter Institute of Industrial Chemistry
C. C. RAILTON, Director, Calico Printers' Association, Ltd.
H. B. SHACKLETON, Messrs. Taylor, Shackleton & Co., Shipley
THOMAS TAYLOR, Cornbrook Chemical Co., Stockport
S. A. H. WHETMORE, British Dyestuffs Corporation, Ltd.
W. J. U. WOOLCOCK, C.E.B., M.P., General Manager, Association British Chemical Manufacturers

Pending the appointment of a permanent chairman, Mr. Percy Ashley, C.B., Assistant Secretary, Industries and Manufactures Dept., Board of Trade, will act as chairman of the committee. The secretary is Mr. W. Graham, M.B.E.

The Melting Point of Diphenylamine¹

By Homer Rogers, W. C. Holmes and W. L. Lindsay

E. I. DU PONT DE NEMOURS & CO., WILMINGTON, DELAWARE

Diphenylamine has become a product of very considerable commercial importance, by reason of its extensive use in the explosive and dye industries. During the war, the specifications of the United States Government called for diphenylamine of a melting-point range between 52° and 54° C., thereby implying that the latter temperature was the melting point of the pure material. As experience had indicated that 54° was probably too high a figure for this constant, it seemed desirable to determine the melting point of pure diphenylamine very exactly.

The temperature generally quoted in literature as the melting point of diphenylamine has been 54° C., the first authorities for which were Merz and Weith.² They stated that previous to their work in 1873, the accepted figure for diphenylamine had been 45° C., which temperature was obtained by Hofmann³ in 1864. The purity of the product which Merz and Weith used was tested by analysis for carbon and hydrogen. They gave no details of their methods of preparing their pure product or determining its melting point.

The following reference works, which include almost without exception the authorities to which one would turn for dependable information on the subject, give 54° C. as the melting point:

Beilstein, "Handbuch der Organischen Chemie"
Meyer and Jacobsen, "Lehrbuch der Organischen Chemie"
Richter, "Lexikon der Kohlenstoffverbindungen"
Landolt-Börnstein, "Physikalisch-Chemische Tabellen"
Watts, "Dictionary of Chemistry"
Thorpe, "Dictionary of Applied Chemistry"
Sidgwick, "Organic Chemistry of Nitrogen"
Allen, "Commercial Organic Analysis"

In addition, the figure is quoted in such generally used textbooks of organic chemistry as those by Richter, Bernthsen, Cohen, Holleman, and Molinari.

In spite of the impressiveness of the above list of references, it is interesting to note that in all cases where any authority is cited for the figure 54° C. the reference is to Merz and Weith.

Matignon and Deligny,⁴ in 1897, found the melting point to be 54.2° C. Stillman and Swain,⁵ in 1899, determined the melting point as 54°.

All the published determinations since that time, however, to the best of our knowledge, point to a lower temperature than 54° for the melting point. Bogojawlenski⁶ and Narbutt,⁷ in 1905, by independent determinations, found diphenylamine to melt at 52.85° C. Olsen⁸ quotes this figure. Merck⁹ gives 53.0° C. as the melting point.

Owing to the pressing nature of the question during the war, the investigation of the true melting point

and freezing point of diphenylamine was taken up at two of our research laboratories.

FREEZING POINT

While Merz and Weith mention, and apparently determined, the melting point of diphenylamine, in the tests carried out on diphenylamine to determine whether it meets the specifications the melting point is always determined by the solidification method, and not by means of the familiar capillary tube attached to the bulb of a thermometer and immersed in a liquid bath.

While diphenylamine freezing at 52° C. and higher was successfully manufactured on a large scale, the care required to achieve this result, together with a consideration of the nature of the impurities likely to be present, led us to doubt whether absolutely pure diphenylamine could have a freezing point as high as 54° C., especially since in a previous investigation with a similar object the purest material obtained froze at 52.85° C. It was, therefore, decided to undertake the preparation of absolutely pure diphenylamine, either by purification of the commercial product or by some synthetic method, and to establish its true freezing point beyond doubt. This program was not carried to completion because of the relatively slight importance of the subject after the signing of the armistice, and while the work thus fell short of our original intention of establishing the true freezing point exactly, we have considered it worth while to publish our conclusions as far as they go, together with the most important data on which these conclusions are based. Our conclusion is that pure diphenylamine has a freezing point within a few hundredths of a degree of 53° C. Our evidence in support of this view is summarized briefly below.

CRYSTALLIZATION—Our purest diphenylamine was obtained by repeated crystallization of the commercial product. A number of solvents were examined as regards their suitability, including acetone, carbon disulfide, carbon tetrachloride, ether, benzene, toluene, xylene, aniline, and nitrobenzene, in all of which diphenylamine is highly soluble at room temperature; methanol, ethyl alcohol, isopropyl alcohol, normal butyl alcohol, dimethylaniline, and acetic acid, in which saturation is reached at room temperature with a diphenylamine concentration of 20 to 40 per cent; and the paraffin hydrocarbons, most of which dissolve less than 20 per cent at room temperature. Water was the only liquid tried in which diphenylamine is comparatively insoluble in either the liquid or solid state. The preliminary experiments with these various solvents (including ligroin, used by Merz and Weith) indicated that methanol could be depended upon to give at least as good results as any other, and in all probability better results than most of the solvents listed above. Methanol gave appreciably better and speedier results than any of the aliphatic hydrocarbons

¹ Received December 20, 1920.

² *Ber.*, **6** (1873), 1511.

³ *Jahresb.*, **1864**, 427.

⁴ *Compt. rend.*, **125** (1897), 1103.

⁵ *Z. physik. Chem.*, **29** (1899), 705.

⁶ *Chem. Zentr.*, (1905), II, 945.

⁷ *Z. physik. Chem.*, **54** (1905), 696.

⁸ Van Nostrand's "Chemical Annual," **1918**, 4th Ed.

⁹ "Chemical Reagents, Their Purity and Tests," **1914**, 2nd Ed.

tried. In some experiments it was considered advisable to include crystallizations from petroleum ether in order to remove impurities which might be more soluble in this solvent than in methanol. A typical series of crystallizations will perhaps serve to indicate the progress of the purification. Crude diphenylamine, freezing at $51.7^{\circ}\text{C}.$, was crystallized five times from methanol, the product at this point freezing at $52.95^{\circ}\text{C}.$ Crystallization of this product from petroleum ether raised the freezing point to $53^{\circ}\text{C}.$ Two more crystallizations from petroleum ether failed to raise the freezing point. Crystallization from methanol of the material recovered from the fifth crystallization from methanol also gave material freezing at $53^{\circ}\text{C}.$ In another series the crude material was distilled, then crystallized from methanol, distilled and crystallized again, distilled and crystallized a third time, and then crystallized four more times from methanol. The second of these four crystallizations brought the freezing point to $53^{\circ}\text{C}.$, but the two subsequent crystallizations failed to increase it. It is of interest also to note that the material recovered by evaporation of the mother liquor from the last crystallization froze at $52.98^{\circ}\text{C}.$ All the temperatures were measured with a carefully calibrated thermometer and are corrected for stem emergence. While the work on crystallization included many experiments, the above results are typical of the best obtained and were based on a considerable amount of preliminary work.

DISTILLATION—In addition to the crystallization experiments, distillation with a column was tried as an alternative method of purification. After many preliminary distillations in glass, an iron column was finally constructed. In a typical distillation with this column, about 16 kilos of crude diphenylamine gave fractions freezing at from 51.35° up to $52.5^{\circ}\text{C}.$, and then down again to $49.3^{\circ}\text{C}.$ The fraction freezing at $52.5^{\circ}\text{C}.$ amounted to 600 g. (about 3.7 per cent of the total). The temperatures were not recorded in this run. In a typical distillation in glass, a fraction freezing at $52.5^{\circ}\text{C}.$ distilled over a range of 0.5° . The material used in this distillation was a fraction, freezing at $52.2^{\circ}\text{C}.$, obtained in a previous fractionation in glass.

OTHER METHODS—Various other lines of work, started with the object of confirming the results described above, either gave products freezing well below $53^{\circ}\text{C}.$ or were discontinued because of the decreasing importance of the subject. Among these were attempts to synthesize diphenylamine by unusual methods, none of which gave a product freezing above $53^{\circ}\text{C}.$, even after careful crystallization, and a synthesis by the usual aniline salt method, starting with benzene purified with extreme care, and purifying the intermediate products and reagents by the best methods available in the literature. The crude material obtained from this latter synthesis, after simple steam distillation, froze at $52.8^{\circ}\text{C}.$ Crystallization from petroleum ether raised it to $52.85^{\circ}\text{C}.$, and a second steam distillation and crystallization from petroleum ether to $52.95^{\circ}\text{C}.$, at which point the work was discontinued.

From a consideration of the results obtained as above, we have concluded that the freezing point of pure diphenylamine is within a few hundredths of a degree of $53^{\circ}\text{C}.$ and that the results of Merz and Weith cannot be accepted as the true freezing point (or true melting point) of pure diphenylamine. If the true freezing point were $54^{\circ}\text{C}.$, our purest product must have contained more than 1 per cent of an impurity with a molecular weight of not less than 100, or more than 2 per cent of an impurity with a molecular weight equal to that of diphenylamine. It would require almost 3 per cent of triphenylamine to lower the freezing point by $1^{\circ}\text{C}.$ It seems probable that Merz and Weith determined the melting point by the ordinary capillary method, which is known to give high results unless made with extreme care. Without attempting to review the literature completely on the physical constants of diphenylamine, attention may be called to an abstract of an article by Vassilief,¹ giving the melting point of diphenylamine as $53.2^{\circ}\text{C}.$ Unfortunately, the original article, which so far as we know contains the most recently published data in this connection, appeared in a Russian journal which is not available to us.

In addition to the above data on our own preparations, freezing and melting points were determined on various purchased samples, as follows:

	Freezing Point $^{\circ}\text{C}.$	Melting Point		
		Sweating Point $^{\circ}\text{C}.$	Meniscus Point $^{\circ}\text{C}.$	Clear Point $^{\circ}\text{C}.$
Merek & Co.....	52.85	52.95	53.05	53.10
A. H. Thomas Co.....	52.85	...	52.75	...
A. H. Thomas Co., twice crystallized from methanol.....	52.85			
Kahlbaum.....	...	52.15	52.55	52.85
Eimer and Amend.....	...	51.65	52.15	52.65

All temperatures were determined with a standard thermometer and are corrected for stem emergence. The Kahlbaum and the Eimer and Amend samples were too small for a freezing-point determination.

The following work was done at another laboratory.

The diphenylamine used for the tests was washed once with distilled water, to which a small amount of hydrochloric acid had been added. It was then thoroughly washed five times with hot distilled water, crystallized five times from ethyl alcohol, and dried by prolonged heating in a drying oven at a temperature slightly below the melting point.

Determinations of the solidification point were made on this material, and purity was considered to be established when the crystals from three successive crystallizations gave identical solidification points, within the limits of experimental accuracy. The diphenylamine to be tested was placed in a wide-mouthed test tube, which was inserted through a tightly fitting rubber stopper in a bottle of about 500 cc. capacity. The bottle was then partially evacuated. The solidification point was obtained by the usual method of warming the diphenylamine until all was melted, then allowing to cool, careful observation being made of the temperature at which solidification took place. A thermometer was immersed in the molten diphenylamine during the cooling, and the liquid was

¹ Bull. soc. chim., 16, 182.

stirred vigorously meanwhile with a glass stirrer. The temperature fell slowly during the cooling until solidification began to take place, at which point the temperature remained stationary for a few minutes or rose slightly. The solidification point was taken at the highest point of the rise in temperature, or at the point where the temperature remained stationary for a brief time. If the temperature is read at definite intervals of time during the cooling and solidification, as every 15 or 30 sec., and the observations are plotted on a curve, temperature against time, the solidification point is very evident.

Working as described above, the following determinations were made and checked for the solidification point of diphenylamine, no determination being made before the material from the fifth crystallization had been obtained.

SAMPLE	SOLIDIFICATION POINT ° C.
5th Crystallization.....	52.94
5th Mother Liquor Evap.....	52.75
6th Crystallization.....	52.93
7th Crystallization.....	52.96
7th Mother Liquor Evap.....	52.96

In the determination of the solidification point, the thermometer was immersed in the diphenylamine to a depth of about 3 in. As the exposed portion of the thermometer was partly within the open test tube and partly unenclosed, two separate corrections for emergent thread were used, the total correction being, of course, the sum of the two. This same diphenylamine, on which a solidification point of 52.96° C. had been obtained, was tested for melting point by the capillary tube method, and found to melt at the same point as the first lot of material, 53.05° C. The pure product was white in color with a mild pleasant odor.

MELTING POINT

The material used as a starting point for preparing pure diphenylamine was a sample of good commercial product, of a light yellow color, melting at 52.05° C. The crude material was purified as follows:

Five hundred grams of the diphenylamine were thoroughly washed with hot distilled water five times, the water being decanted off between treatments. The material was then crystallized five times from ethyl alcohol, the crystals being freed from the mother liquor each time by use of a Büchner funnel. They were thoroughly dried in the air at a slightly elevated temperature, and then vacuum-dried over calcium chloride. The purification of the diphenylamine was assumed to be complete at this point, as the melting points of the dried crystals and of the residue obtained by the evaporation of the mother liquor were the same, 53.05° C.

The determinations of the melting point were made by the capillary tube method, thin-walled tubes being prepared by drawing out 12-cm. glass tubing. It seemed desirable that the capillary tubes should have an outside diameter of not more than 1.0 mm., as this had been shown to be a satisfactory diameter in previous experiments. As the heat of fusion of diphenylamine is 26.3 cal. per g. it is more than usually important that the temperature of the bath be increased at a very slow rate.

The individual determinations are recorded below:

SAMPLE	Rate of Rise of Temp. of Bath	Diameter of Capillary Tubes Mm.	Melting Point ° C.
Original Material.....	1° in 3 min.	1.0	52.05
After washing with water.....	1° in 6 min.	0.6	52.2
1st Cryst.....	1° in 3 min.	1.0	52.8
1st Cryst.....	1° in 3 min.	1.0	52.8
2nd Cryst.....	1° in 3 min.	1.0	52.9
2nd Cryst.....	1° in 3 min.	1.0	53.0
3rd Cryst.....	1° in 3 min.	1.0	53.05
3rd Cryst.....	1° in 3 min.	1.0	53.1
4th Cryst.....	1° in 6 min.	0.8	53.0
4th Cryst.....	1° in 6 min.	1.0	53.05
4th Cryst.....	1° in 6 min.	0.8	53.1
4th Cryst.....	1° in 6 min.	0.6	53.0
4th Cryst.....	1° in 10 min.	0.9	53.05
4th Cryst.....	1° in 10 min.	0.6	53.0
4th Cryst.....	1° in 10 min.	0.6	53.0
4th Cryst.....	1° in 10 min.	0.9	53.05
4th Mother Liquor Evap.....	1° in 6 min.	0.6	52.9
4th Mother Liquor Evap.....	1° in 6 min.	0.8	52.85
4th Mother Liquor Evap.....	1° in 6 min.	0.8	52.85
4th Mother Liquor Evap.....	1° in 6 min.	0.6	52.9
5th Cryst.....	1° in 6 min.	0.8	53.05
5th Cryst.....	1° in 6 min.	1.0	53.1
5th Cryst.....	1° in 7 min.	1.0	53.05
5th Cryst.....	1° in 10 min.	0.9	53.05
5th Cryst.....	1° in 15 min.	0.8	53.0
5th Cryst.....	1° in 20 min.	1.0	53.05
5th Cryst.....	1° in 20 min.	1.0	53.05
5th Cryst.....	1° in 20 min.	0.8	53.0
5th Cryst.....	1° in 20 min.	1.4	53.05
5th Mother Liquor Evap.....	1° in 20 min.	1.0	53.05
5th Mother Liquor Evap.....	1° in 20 min.	1.0	53.05

The melting point was taken at the point at which the diphenylamine within the capillary tube became absolutely clear and transparent, without any suspended, unmelted crystals apparent. The majority of the above determinations on the final product showed 53.05° C. as the melting point, especially those determinations which were carried out most carefully.

In order to eliminate as far as possible any error that might be introduced through the inaccuracy of the thermometer, two standard thermometers were used in checking the determination, one standardized by the U. S. Bureau of Standards and the other by the Physikalische-Technische Reichsanstalt. These thermometers were found to check one another exactly after applying the corrections furnished by these authorities. The accuracy of their standardizations was checked also by redetermination of their respective ice points. Corrections for temperature of emergent stem were made throughout.

SUMMARY

The temperature generally quoted in the standard reference works for the melting point of diphenylamine is 54.0° C. All published determinations made within the last 15 yrs., however, indicate a lower temperature than 54° C. for the melting point.

Careful determinations on thoroughly purified material, using standardized thermometers, have shown the pure material to have a melting point of 53.0° C. Two separate investigations of the freezing point gave results of 52.96° and 53.00° C.

Platinum Theft

During the night of Monday, February 14, 1921, three platinum crucibles were taken from the laboratory of the Pacific Coast Steel Co., San Francisco, Cal.

Two of these crucibles were marked Baker & Company, and weighed 12.1592 and 12.1617 g., respectively. The third was marked W and weighed 11.6668 g.

The Activity of Phytase as Determined by the Specific Conductivity of Phytin-Phytase Solutions^{1,2}

By F. A. Collatz and C. H. Bailey

DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION, ST. PAUL, MINNESOTA

The activity of phytase has commonly been measured by determining the quantity of inorganic compounds of phosphoric acid produced by the hydrolysis of phytin. The early studies of this enzyme by Suzuki, Yoshimura, and Tokaishi³ were occasioned by the appearance of phosphoric acid or its salts in a mixture of rice bran and water. Vorbrodtt⁴ studied the activity at different temperatures of phytase prepared from barley, and concluded that it reached a maximum in the neighborhood of 28° C. At temperatures of 58° to 60° the action was found to be

Since the principal object of these experiments was to determine the influence of temperature upon the activity of phytase, time and temperature were the only variables studied. The temperatures employed ranged by 5° intervals from 25° to 60° C. A water solution of purified phytin¹ was used as the substrate. The active phytase was prepared by digesting finely ground wheat bran with water at a temperature of 2° to 3° C., and precipitating the enzyme by filtering into 95 per cent alcohol. The precipitate was dried, dissolved in water, and reprecipitated with alcohol.

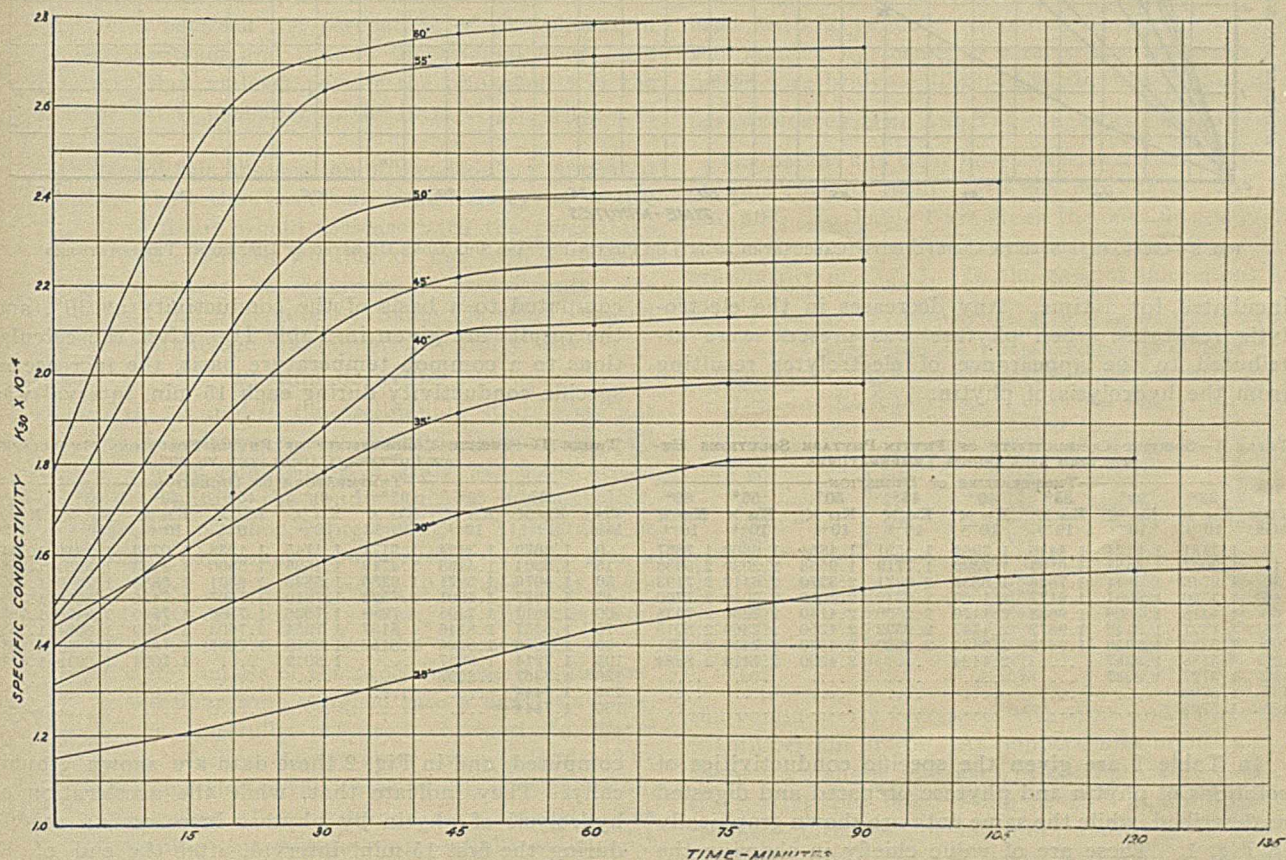


FIG. 1—GRAPHS SHOWING EFFECT OF HYDROLYSIS OF PHYTIN BY PHYTASE AT DIFFERENT TEMPERATURES UPON CONDUCTIVITY OF SOLUTIONS

slow, while boiling stopped the formation of phosphoric acid.

Since phosphoric acid or its salts are end-products of the hydrolysis of phytin, and are ionized more in water solution than the original phytin, the electrolytic resistance of the solution of phytin and phytase should afford a measure of the activity of the latter.

¹ Received December 1, 1920.

² Published with the approval of the Director, as Paper No. 212, Journal Series, Minnesota Agricultural Experiment Station.

³ "Über ein Enzyme 'Phytase' das 'Anhydro-oxymethylene-di-phosphorsäure' spaltet," Tokyo Imperial Univ. College of Agriculture, *Bulletin* 7 (1907), 503.

⁴ "Untersuchungen über die phosphorverbindungen in den Pflanzensamen mit besonderer Berücksichtigung des Phytins," *Bulletin Int. de l'Acad. Sci. Cracovie*, Serie AI (1910), 414.

This was repeated several times, the precipitate dried at room temperature *in vacuo*, and finely pulverized in a mortar, yielding a grayish white powder.

Solutions of phytin and of the active phytase preparations were prepared by dissolving 50 mg. of each in separate 50-cc. portions of water. These were brought to the desired temperature, equal volumes were mixed in a Freas conductivity cell, and the electrolytic resistance determined at once, and again every 15 min. until successive readings were alike or nearly so. It was found that when phytin and water were mixed in the absence of active phytase, no change occurred in the electrolytic resistance of the solution when

¹ This phytin was kindly supplied by Dr. J. B. Rather

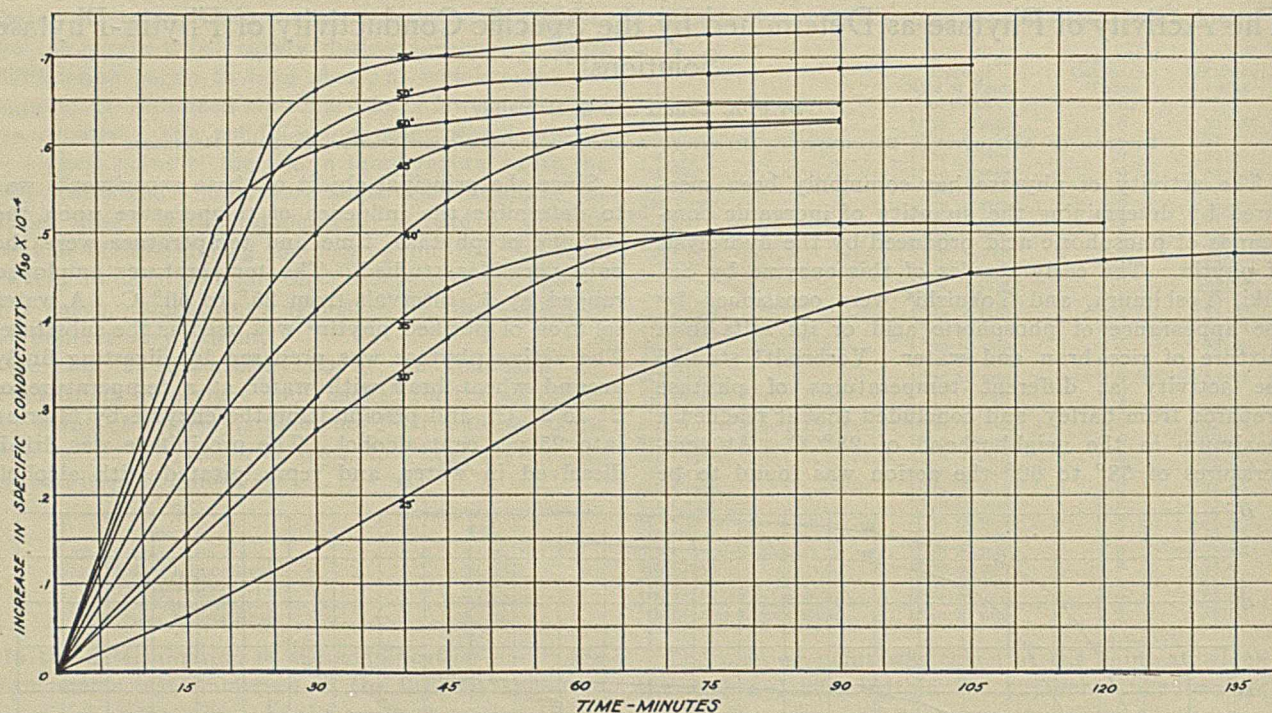


FIG. 2—INCREASE IN SPECIFIC CONDUCTIVITY (CALCULATED TO 30°) OF PHYTIN-PHYTASE SOLUTIONS DIGESTED AT DIFFERENT TEMPERATURES

incubated for a time. Any decreases in the electrolytic resistance when phytase was present were attributed to the appearance of electrolytes resulting from the hydrolysis of phytin.

computed to a basis of the conductivity at 30°, and the results are given in Table II. After the calculations to a common temperature basis, the increase in specific conductivity during each 15-min. interval was

TABLE I—SPECIFIC CONDUCTIVITY OF PHYTIN-PHYTASE SOLUTIONS HYDROLYZED AT VARIOUS TEMPERATURES

TIME Min.	TEMPERATURE OF DIGESTION							
	25° $K_{25} \times 10^{-4}$	30° $K_{30} \times 10^{-4}$	35° $K_{35} \times 10^{-4}$	40° $K_{40} \times 10^{-4}$	45° $K_{45} \times 10^{-4}$	50° $K_{50} \times 10^{-4}$	55° $K_{55} \times 10^{-4}$	60° $K_{60} \times 10^{-4}$
0	1.1481	1.3124	1.4416	1.3964	1.4551	1.4854	1.6660	1.7887
15	1.2047	1.4488	1.6109	1.7390	1.7719	1.9556	2.2090	2.5933
30	1.2746	1.5871	1.7825	1.8832	2.0921	2.3270	2.6410	2.7193
45	1.3526	1.6901	1.9177	2.1063	2.2212	2.4010	2.7010	2.7700
60	1.4318	1.7508	1.9688	2.1170	2.2506	2.4140	2.7230	2.7938
75	1.4821	1.8146	1.9872	2.1347	2.2592	2.4250	2.7360	2.8015
90	1.5282	1.8226	1.9872	2.1424	2.2620	2.4330	2.7410	2.8271
105	1.5588	1.8257	2.1424	2.4380	2.7410	2.8384
120	1.5727	1.8257
135	1.5796
150	1.5796

TABLE II—SPECIFIC CONDUCTIVITY OF PHYTIN SOLUTIONS HYDROLYZED BY PHYTASE, CALCULATED TO 30°

TIME Min.	TEMPERATURE OF DIGESTION							
	25° $K_{25} \times 10^{-4}$	30° $K_{30} \times 10^{-4}$	35° $K_{35} \times 10^{-4}$	40° $K_{40} \times 10^{-4}$	45° $K_{45} \times 10^{-4}$	50° $K_{50} \times 10^{-4}$	55° $K_{55} \times 10^{-4}$	60° $K_{60} \times 10^{-4}$
0	1.2679	1.3124	1.3171	1.1745	1.1338	1.0780	1.1316	1.1416
15	1.3304	1.4488	1.4719	1.4626	1.3800	1.4193	1.5004	1.6551
30	1.4076	1.5871	1.6286	1.5839	1.6301	1.6888	1.7939	1.7355
45	1.4937	1.6901	1.7522	1.7610	1.7307	1.7426	1.8346	1.7680
60	1.5811	1.7508	1.7989	1.7806	1.7536	1.7520	1.8496	1.7832
75	1.6367	1.8146	1.8157	1.7954	1.7603	1.7600	1.8584	1.7883
90	1.6876	1.8226	1.8157	1.8019	1.7625	1.7657	1.8618	1.8043
105	1.7214	1.8257	1.8019	1.7694	1.8618	1.8115
120	1.7367	1.8257
135	1.7444
150	1.7444

In Table I are given the specific conductivities of solutions of phytin and phytase prepared and digested as described, while the same data are shown graphically in Fig. 1. These are of value chiefly in showing the rate of hydrolysis at the several temperatures, and indicate that as the temperature is elevated the reaction is accelerated and reaches completion more quickly.

The data in Table I are of limited value, since the conductivity in each series was determined at the temperature of incubation. To make the data comparable it was necessary to calculate the conductivity of the several series to a common temperature basis. To this end, a solution was digested at 55° until hydrolysis ceased. Its conductivity was determined at 55°, and, after cooling, was redetermined at 25°. The difference between the two readings indicated an increase in conductivity of 1.89 per cent for each degree of increase in temperature. All of the data were then

computed, and in Fig. 2 these data are shown graphically. They indicate that, while the acceleration of hydrolysis of phytin by phytase increases up to 60° during the first 15-min. interval, after the end of 15 min. the rate diminishes when the temperature exceeds 55°. Thus the increases in the conductivity of the mixtures digested at 50° and at 55° were greater at the end of 30 min. than in the mixtures digested at 60°.

SUMMARY

Changes in the specific conductivity of a water solution of phytin and phytase afford a convenient measure of the progress of the hydrolysis of phytin. The phytase prepared from wheat bran appeared to effect a more complete hydrolysis of the phytin at a temperature of about 55° than at any other temperature, although hydrolysis proceeded more rapidly at 60° during the first 15 min. As the temperature is increased the reaction reaches completion more quickly.

Studies of Wheat Flour Grades. I—Electrical Conductivity of Water Extracts^{1,2}

By C. H. Bailey and F. A. Collatz

DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION, ST. PAUL, MINNESOTA

The ash content of wheat flour is almost universally employed at the present time as an index of grade. High-grade or patent flours contain the least ash, occasionally as low as 0.35 per cent, while the lower or clear grades sometimes contain over 2 per cent. These differences are due to the fact that the lower grades contain more of the branny and embryo structures, which structures contain a higher percentage of ash than the floury portion of the wheat kernel.

Swanson³ determined the ratio of total to water-soluble phosphorus in different streams and grades of commercial flours. He found that when the flour was extracted with water at 40° there was generally a parallelism between the percentage of phosphorus in the water extract and that in the original flour. He suggested that at least part of the phosphorus in the flour extract is probably in the form of phosphates of potassium.

In view of this observation of Swanson's, it appeared probable that the electrical conductivity of water extracts of flours would increase with the percentage of ash. To ascertain whether or not such a relation existed, a series of preliminary experiments was conducted, and in a note by Bailey⁴ it was indicated that the parallelism was apparently fairly exact.

METHOD OF STUDY

The data secured in the preliminary study were not adequate for drawing any definite conclusions, and recently a more comprehensive study was made of the factors determining the conductance of such extracts. Two samples of flour, representing a high-grade or patent flour containing 0.43 per cent of ash, and a clear or lower grade containing 0.92 per cent, were extracted with conductivity water at different temperatures, and for various lengths of time.

The general details of the procedure were as follows: 10 g. of the flour were weighed into a dry Jena flask, and 100 cc. carefully prepared conductivity water having the desired temperature were added. The flour was suspended in the water by vigorous agitation, care being taken that no lumps were formed. The flask containing this mixture was partially submerged in a water thermostat, which was maintained at the desired temperature. The flour was kept in suspension by intermittent shaking during the extraction period, and was then thrown out of suspension by whirling for 5 min. in a centrifuge. The clear decantate was passed through a filter to remove any floating particles, and its electrical conductivity determined.

APPARATUS FOR CONDUCTIVITY MEASUREMENTS

A special dip electrode was employed, which was similar to the ordinary Freas cell with the bottom cut off. The glass walls of the cell extended far enough

below the platinum electrodes to protect them from mechanical injury. In using this cell, the extract was placed in a glass vial and brought to temperature (30°), and the electrodes were then immersed in the contents of the vial. This made it possible to work rapidly by transferring the dip electrode from one vial to another. In actual practice it was found advisable to place portions of the extract in at least two vials, in the first of which the electrode was rinsed off, while the measurements were made with the electrode in the second of the two vials.

A constant speed, high frequency generator furnished a current of 1000 alternations per second, which was used with a tunable telephone receiver. A balance was secured by means of a resistance box, and a 10-meter wire bridge calibrated in the middle for 50 cm.

INFLUENCE OF TIME AND TEMPERATURE OF EXTRACTION

The patent and clear flours were extracted for periods of time ranging from 15 to 960 min. at 0°, 25°, 40°, and 60°. In Table I are given the specific conductivities of the extracts thus prepared, data which are given graphically in Fig. 1. In the case of the patent flour

TABLE I—SPECIFIC CONDUCTIVITY ($K_{30} \times 10^{-4}$) OF THE WATER EXTRACTS OF PATENT AND CLEAR FLOURS EXTRACTED AT DIFFERENT TEMPERATURES FOR DIFFERENT LENGTHS OF TIME

Time of Extraction Min.	TEMPERATURE OF EXTRACTION			
	0° $K_{30} \times 10^{-4}$	25° $K_{30} \times 10^{-4}$	40° $K_{30} \times 10^{-4}$	60° $K_{30} \times 10^{-4}$
	<i>Patent Flour</i>			
15	5.478	5.797	6.161
30	4.601	5.590	5.916	6.253
60	4.600	5.668	5.958	6.272
120	5.264	5.798	6.110	6.347
240	5.515	5.830	6.181	6.444
480	5.609	5.950	6.211	6.443
960	5.780	5.957
	<i>Clear Flour</i>			
15	8.789	9.355	9.780
30	6.477	9.167	9.880	9.872
60	6.770	9.367	10.018	9.936
120	7.378	9.999	10.260	10.182
240	8.041	10.160	10.347	10.195
480	8.890	10.401	10.680	10.474
960	9.333	10.593	10.770	10.474

the conductivity increased with time and temperature within certain limits. At temperatures of 40° and 60° there were slight increases in conductivity of the extract after 240 min., while at 25° equilibrium was reached at the end of 480 min., and at 0° it was not reached until after at least 960 min. Moreover, there was a difference in the shape of the curves at the four temperatures. As the temperature increased the initial rise in conductivity per unit of time became more abrupt, but equilibrium was reached much sooner, and the curve consequently flattened out in a shorter time.

The clear flour gave somewhat different results. Equilibrium was not reached so quickly at any of the temperatures, and what is even more significant, the conductivities of the extracts prepared at 60° were lower, with the exception of the one taken at the end of 15 min., than were extracts prepared at 40°. Thus the values at 60° were intermediate between the 25° and 40° extracts.

The explanation of these curves is probably to be

¹ Received December 1, 1920.² Published with the approval of the Director, as Paper No. 213, Journal Series, Minnesota Agricultural Experiment Station.³ THIS JOURNAL, 4 (1912), 274.⁴ Science, 47 (1918), 645.

found in the conclusions reached from observations made on phytase activity. In the preceding paper by Collatz and Bailey¹ the progress of the hydrolysis of phytin by phytase was discussed, and data were presented showing much the same response to temperature as is exhibited by these flours. Phytase from wheat bran was found to have an optimum tempera-

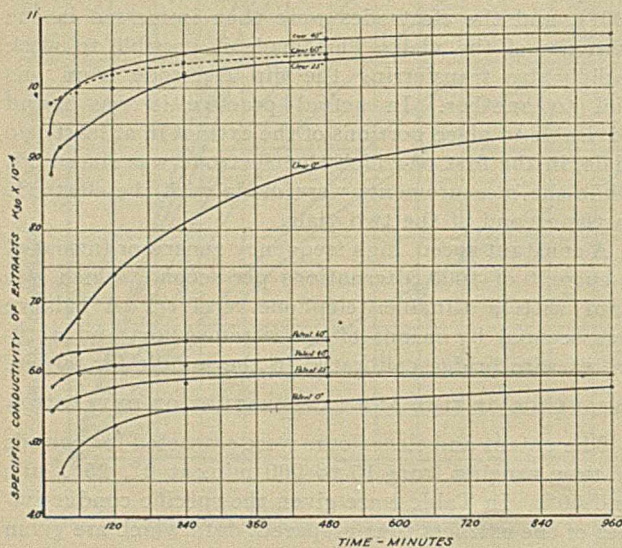


FIG. 1—GRAPHS SHOWING EFFECT OF TIME AND TEMPERATURE OF EXTRACTION OF PATENT AND CLEAR FLOURS UPON SPECIFIC CONDUCTIVITY OF THE EXTRACTS

ture of 55°; the initial rate of change in conductivity of a phytin-phytase solution increased with the temperature, and reached equilibrium more quickly at the higher temperatures. The difference in the behavior of the patent and the clear flours at 60° may possibly be attributed to the ratio of substrate to enzyme in the several grades. From the available data we conclude that the electrolytes of the water extract of wheat flours are chiefly phosphates which are produced as the result of hydrolysis of phytin by the phytase in the natural tissues of the kernel. Since the activity of phytase, and the consequent appearance of electrolytes in the phytase-phytin solution in water, is affected by temperature, and increases to a point of equilibrium with lapse of time, it follows that there are variations in the conductivity of water extracts of any flour dependent upon the conditions of extraction. It is necessary, therefore, to maintain uniform conditions with respect to time, temperature, and ratio of flour to water, in comparing several flours by the electrical conductivity of their water extracts.

ELECTRICAL CONDUCTIVITY OF WATER EXTRACTS OF DIFFERENT FLOUR GRADES

To afford a wide range of quality, and of percentages of ash, the flour streams from two different mills were secured. The series of flours from one mill, designated as Series A, comprised four break flours, and five middlings flours, containing from 0.44 to 1.62 per cent of ash. That from another mill, designated as Series B, included five break flours, a sizings, stone stock, seven middlings, three tailings, and a dust flour, in addition to the patent, first clear, and second clear

flours marketed by the mill. These contained from 0.35 to 1.73 per cent of ash.

The flours in Series A and B were extracted in the ratio of 1 part of flour to 10 parts of water at 25° for 30 min. This temperature was employed primarily because it was easy to maintain. This being about the mean laboratory temperature, it follows that there is little likelihood of significant variation in the temperature of the digest resulting from exposure of the materials either before or after combining the flour and water. The temperature of the mixture consequently changes very slightly during the clarification and filtration processes. It is probable that the deviation from the means observed in the preliminary studies reported by Bailey, in which the flours were extracted at 0°, may be attributed to the varying rate of temperature change in the mixtures from the time they were removed from the ice bath until the clarification was completed. Again, a small variation in the length of the period of extraction results in less error when the extraction is conducted for 30 min. at 25° than when conducted for the same length of time at 0°. Temperatures above 25° are open to the same objections as are those materially lower, namely, the difficulty of maintaining the mixture at a uniform temperature throughout the operation.

TABLE II—RELATION OF SPECIFIC CONDUCTIVITY OF WATER EXTRACTS TO ASH CONTENT OF WHEAT FLOURS

Grade of Flour	Ash Per cent	Specific Conductivity of Water Extract $K_{sp} \times 10^{-4}$
Series A		
First break.....	1.34	10.563
Second break.....	0.59	6.647
Third break.....	0.67	7.690
Fourth break.....	1.62	11.969
First middlings.....	0.44	5.395
Second middlings.....	0.45	5.547
Third middlings.....	0.56	6.338
Fourth middlings.....	1.17	10.242
Fifth middlings.....	0.61	6.777
Series B		
First break.....	0.56	6.508
Second break.....	0.48	5.971
Third break.....	0.58	6.838
Fourth break.....	0.80	8.483
Fifth break.....	0.96	9.167
Sizings.....	0.45	5.564
First middlings.....	0.41	5.270
Second middlings.....	0.38	4.744
Third middlings.....	0.42	5.002
Fourth middlings.....	0.46	5.514
Fifth middlings.....	0.43	5.192
Sixth middlings.....	0.42	5.075
Seventh middlings.....	0.47	5.870
Stone stock.....	0.35	4.643
First fine tailings.....	0.73	7.624
Second fine tailings.....	0.92	8.650
First coarse tailings.....	0.66	7.450
Dust flour.....	1.38	10.610
Patent, 90 per cent.....	0.44	5.815
First clear.....	0.90	8.850
Second clear.....	1.73	12.678

The 30-min. period was selected in order to reduce to a minimum the time involved in completing the determination. A method of grading flour based on the conductivity of the water extract will be more advantageous than the determination of ash only in the event that the time required is materially reduced. If a 30-min. extraction gives comparative results, the reduced time may be more important than increased accuracy accompanying a longer extraction period. From the data presented in the foregoing section it is evident that any procedure is more or less empirical and must be scrupulously followed to afford any basis for comparison.

¹ THIS JOURNAL, 13 (1921), 317.

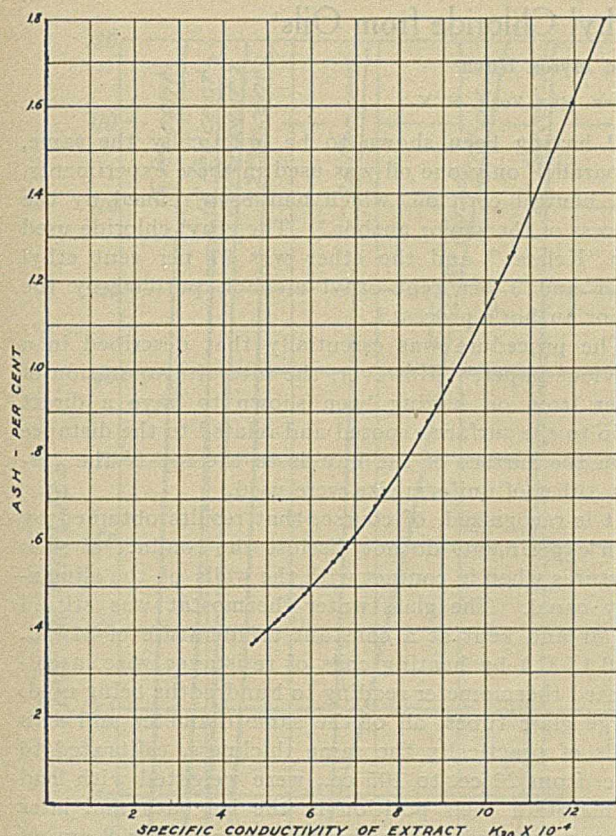


FIG. 2—RELATION OF ASH CONTENT TO SPECIFIC CONDUCTIVITY OF WATER EXTRACTS PREPARED BY EXTRACTING AT 25° FOR 30 MIN.

When the extracts of the thirty flours in the two series were prepared in the manner described, it was found that their specific conductivities varied with the ash content. The variation was not direct, and the curve was not a straight line, but a simple parabola. The ash content and specific conductivity of the flours in Series A and B are given in Table II.

TABLE III—SPECIFIC CONDUCTIVITY OF WATER EXTRACT, ACTUAL AND CALCULATED PERCENTAGE OF ASH IN FLOURS OF SERIES A AND B

SAMPLE	Specific Conductivity of Water Extract $K_{90} \times 10^{-4}$	ASH IN FLOUR		
		Actual Per cent	Calculated Per cent	Difference Per cent
Stone stock.....	4.643	0.346	0.367	+0.021
Second middlings....	4.744	0.378	0.375	-0.003
First middlings.....	5.270	0.409	0.421	+0.012
Sixth middlings.....	5.075	0.417	0.403	-0.014
Third middlings.....	5.002	0.419	0.397	-0.002
Fifth middlings.....	5.192	0.427	0.414	-0.013
Patent ¹	5.590	0.435	0.452	+0.017
First middlings ²	5.395	0.442	0.433	-0.009
Patent.....	5.815	0.442	0.474	+0.032
Second middlings ² ..	5.547	0.446	0.438	-0.008
Sizings flour.....	5.564	0.451	0.449	-0.002
Fourth middlings....	5.514	0.460	0.444	-0.016
Seventh middlings...	5.870	0.467	0.481	+0.014
Second break.....	5.971	0.479	0.492	+0.013
Third middlings ² ...	6.338	0.555	0.534	-0.021
First break.....	6.503	0.564	0.554	-0.010
Third break.....	6.838	0.579	0.597	+0.018
Second break ²	6.647	0.585	0.572	-0.013
Fifth middlings ² ...	6.777	0.613	0.588	-0.025
First coarse tailings..	7.450	0.662	0.683	+0.021
Third break ²	7.690	0.668	0.719	+0.051
First fine tailings....	7.624	0.726	0.709	-0.017
Fourth break.....	8.483	0.803	0.849	+0.045
Clear flour.....	8.850	0.900	0.914	+0.014
Second fine tailings...	8.650	0.919	0.878	-0.041
Clear flour ¹	9.167	0.920	0.973	+0.053
Fifth break.....	9.167	0.955	0.973	+0.018
Fourth middlings ² ..	10.242	1.171	1.196	+0.025
First break ²	10.563	1.340	1.263	-0.077
Dust flour.....	10.610	1.383	1.274	-0.109
Fourth break ²	11.970	1.620	1.606	-0.014
Second clear flour...	12.678	1.731	1.797	+0.066

¹ Flours used in preliminary experiments.

² Series A.

For convenience in comparison, the flours are arranged in Table III in order of their ash content with the specific conductivity in a parallel column. The same arrangement is shown graphically in Fig. 2. In addition, these data have been subjected to mathematical treatment, and the ash content calculated which corresponds to each unit of conductivity on a smoothed curve. In parallel columns are given the results of these calculated percentages, and the differences between the actual and calculated percentages of ash. It will be observed that up to 0.80 per cent of ash the differences are small, being in all but one instance within the limits to be expected in ash determinations. The ratio of conductivity to ash content is sufficiently exact to permit of the determination of the former as an index of flour grade.

SUMMARY

Specific conductivity of the water extracts of wheat flour varies with the time and temperature of extraction. A temperature of 60° or somewhat less gives the highest values.

From the similarity of the response of flour extracts to temperature changes and that of phytin-phytase preparations, it appears that the conductivity of water extracts of wheat flour is due chiefly to inorganic salts of phosphoric acid, resulting from the hydrolysis of phytin through the activity of the enzyme phytase.

When comparisons of different flours are to be made it is necessary that a uniform procedure be followed in the preparation of the extracts.

Specific conductivity of flour extracts parallels ash content and can be employed as an index of flour grade.

In determining the grade of flour by this method it has been found convenient to extract 1 part of flour with 10 parts of water at 25° for exactly 30 min., and measure the conductivity of the clear extract at 30° with a dip electrode.

Standardization of Petroleum Specifications

The Interdepartmental Committee on Standardization of Petroleum Specifications, superseding the war-time committee on the same subject, was organized at its first meeting at the Bureau of Mines, Washington, D. C., February 19, 1921. The committee gave its approval to *Bulletin 5* of the previous committee, continuing in force the specifications on gasoline, kerosene, fuel oils, lubricating oils, signal oils, etc., and decided to adopt the plan of adding a technical subcommittee to handle the details of drawing up and revising specifications and methods of testing. N. A. C. Smith has been appointed chairman of the technical committee. The Committee on Standardization consists of Dr. H. Foster Bain, Bureau of Mines, *Chairman*, representing the Department of the Interior; J. H. Vawter, Office of the Supervising Architect, representing the Treasury Department; Captain Wm. H. Lee, Q. M. C., Office of the Quartermaster General, representing the War Department; E. B. Cranford, Asst. Supt., Division of Post-Office Service, representing the Post-Office Department; B. A. Anderton, Bureau of Public Roads, representing the Department of Agriculture; Dr. C. W. Waidner, Bureau of Standards, representing the Department of Commerce; W. A. E. Doying, Inspecting Engineer, representing the Panama Canal; M. W. Bowen, Assistant to the Chairman, representing the Shipping Board.

The Rate of Evaporation of Ethyl Chloride from Oils¹

By Charles Baskerville and Myron Hirsh²

COLLEGE OF THE CITY OF NEW YORK, NEW YORK, N. Y.

The determination of the rate of evaporation of ether from various oils³ gave the foundation of ether-oil colonic, and later oral, anesthesia introduced by Gwathmey,⁴ and since extensively used by a number of surgeons and specialists with gratifying success.⁵ In particular cases analgesia is preferred to anesthesia, in so far as the one may be caused to prevail. Analgesia is evident previous to anesthesia during induction and obtains as the patient comes out of the stage of full anesthesia, the period of analgesia varying in time and degree with the drug administered, rate of administration, body saturation, and rate of elimination. Analgesia is desirable in minor short, as well as prolonged, operations in dentistry, when recourse need not be had to anesthesia. Analgesia, without anesthesia, offers opportunity for comfortable dressing of serious wounds. Prolongation of post-anesthetic analgesia reduces the necessary time of anesthesia for the sewing of the incision; and the dressing may be done during that period.

Cocaine, stovaine, novocaine, and this general class of drugs are most useful for such purposes, being applied in various ways, but their use is always attended unhappily with an element of uncertain idiosyncrasy.

Ethyl chloride in quantity is about six times as strong (this term being used for lack of a better) as ethyl ether, and when judiciously administered produces prolonged pre- and post-anesthetic analgesia. Furthermore, its physiological action is less accompanied with the variegated hallucinations always evident in patients to whom nitrous oxide is administered. At the suggestion of Dr. J. T. Gwathmey, the senior author's medical colleague in all his researches on anesthesia,⁶ an investigation was undertaken on the rate of evaporation of ethyl chloride from oils and mixtures of ethyl chloride and ether from oils with the view of using the results as a basis for inducing analgesia, or prolonging it in conjunction with anesthesia, for the purposes indicated above.

The mutual solubility of ethyl chloride and oils presented nothing novel, but the physical properties of the former (b. p. 12.5° C.) indicated probable marked variations in rate of evaporation from that of ethyl ether (b. p. 34.6° C.). On account of the extremely rapid evaporation of ethyl chloride at ordinary room temperatures, all mixtures were prepared cold, after containers and constituents had been chilled by melting ice.

The rate of evaporation of ethyl ether from different

oils¹ having been shown to be practically the same, or parallel, only one oil was used in these experiments, viz., neutral corn oil, which had been refined by the process of the senior author.² The ethyl chloride used was "Kelene," and the ether was 97 per cent ethyl ether and 3 per cent ethyl alcohol, purified by the senior author's process.³

The procedure was essentially that described in a previous paper.¹ However, the rate of evaporation of ether from oil having been shown to have a direct ratio to the surface exposed and related to the distance from the surface of the liquids to the top of the vessels, tubes of uniform size were used.

It is recognized, of course, that results obtained by such experiments do not disclose the conduct of such mixtures when in contact with the walls of the alimentary canal. The glass water thermostat was stirred by air and kept at a constant temperature of 37° C. ($\pm 0.1^\circ$ C.) by heating coils of resistance wire, a calibrated thermometer reading to hundredths being used. Large glass tubes, all of the same diameter and with walls of practically the same thickness, calibrated to 1 cc. from 20 cc. to 105 cc., were weighted with lead to maintain their position in the ice bath and later when suspended in the thermostat to within 8 cm. of the tops.

During the first 5 min. after the tubes were placed in the thermostat, readings were taken every minute to determine the maximum volume expansion up to 37° C. After that, readings were made every 5 min. for 2 or 3 hrs.

The mixtures by volume, measured at the temperature of melting ice, are shown in the accompanying chart, which gives a graphic representation of the results obtained. The abscissae show the number of cc. of ethyl chloride evaporated from the oil mixture, and the ordinates the time of evaporation. The experiments offering results of value in connection with our particular object were verified by frequent repetition.

The mixtures containing 25 per cent or more ethyl chloride by volume boiled vigorously during the time the temperature rose to 37° C. The use of such mixtures for internal administration was obviously out of question. However, it was determined that the rate of evaporation of ethyl chloride from oil quickly acquires a definite and fairly fixed speed, which begins when the solution has acquired a volume composition of 13 to 14 per cent of ethyl chloride. If an original mixture of 15 per cent be used, the uniform speed is established within 10 min. for surface exposures obtaining in the experiments.

APPLICATION TO USE IN ANESTHESIA

These facts may later prove to be of moment in ethyl chloride-oil alimentary administration, for, as mentioned above, 5 cc. of ethyl chloride are equivalent

¹ Presented before the Division of Medicinal Products Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

² Du Pont Scholar, College of the City of New York.

³ *Am. J. Surgery*, January 1916; *Proc. Am. Phil. Soc.*, August 1915.

⁴ International Medical Congress, London, 1913; "American Year Book of Anesthesia and Analgesia," 1915.

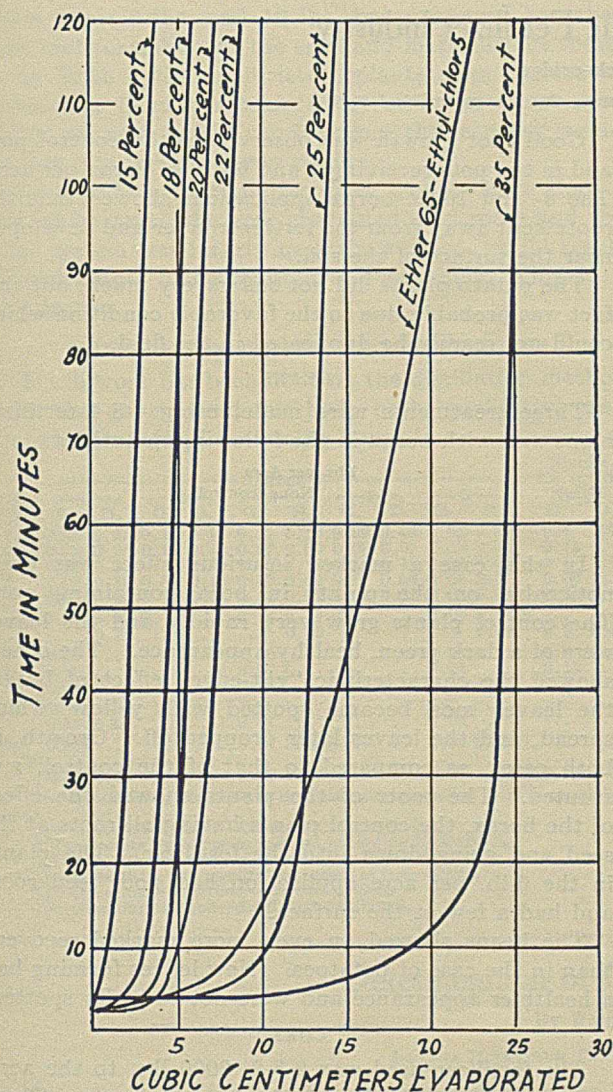
⁵ Gwathmey and Karsner, *J. Am. Med. Assoc.*, 70 (1918), 993; *Brit. Med. J.*, March 2, 1918; Ficklen, *N. O. Med. J.*, January 1920; Lathrop, New Orleans Meeting, A. M. A., and others.

⁶ Gwathmey and Baskerville, "Anesthesia," D. Appleton & Co.

¹ *Loc. cit.*

² *J. Frank. Inst.*, June 1916.

³ Baskerville and Hamor, *THIS JOURNAL*, 3 (1911), 302.



to 30 cc. of ether as an inhalation anesthetic, although animal experimentation carried out by Drs. J. T. Gwathmey and G. B. Wallace in the Bellevue Laboratories, New York, with ethyl chloride-oil colonic administration, have not so far been encouraging; yet most satisfactory results have been obtained in dental surgery by Dr. M. Ecker in coöperation with Dr. Gwathmey. The technique is very simple. A vessel containing an 18 per cent ethyl chloride mixture is interposed in the train of the nitrous oxide-oxygen mixture on its way to the patient. Just enough ethyl chloride vapor is picked up by passing over about 5 cm. of the ethyl chloride mixture to induce analgesia for the extraction of teeth without the patient having experienced the excitement stage just prior to surgical anesthesia, so noticeable in the use of nitrous oxide. As only a few hundred cases of humans have been so treated up to date, even though with the most gratifying success, it is too soon to draw conclusions. However, sufficient data were accumulated to warrant a study of the keeping qualities of such mixtures as might prove to be most useful in dental surgery. The insertion of anesthol (ether, 47.1; ethyl chloride, 17; chloroform, 35.89 per cent) in the train has proved most successful in about 4000 cases.

Oil solutions containing 18 to 22 per cent ethyl chloride lose one-fourth to one-half of the volatile constituents upon standing for one week at room temperature in loosely stoppered bottles, which are occasionally opened for a few minutes. Hence, such ethyl chloride-oil mixtures must be tightly closed or kept in a refrigerator to prevent changes in proportions. In fact, it is advisable to make up such solutions immediately before use so that the anesthetist may know the quantity of anesthetic he is administering.

ETHYL CHLORIDE-ETHER-OIL MIXTURES

As oil-ether (usually 25:75) has proved to be such a valuable adjunct to the comfort of the patient in operations and dressings, by either colonic or oral administration,¹ and as ethyl chloride exhibits such desirable analgesic effects, a mixture of oil, ether, and ethyl chloride was prepared and the comparative rate of evaporation determined. For reasons already indicated above, the mixture was made up of oil, 30 per cent; ether, 65 per cent; and ethyl chloride, 5 per cent. The curve obtained is plotted on the chart. As yet clinical data are not available for drawing any conclusions.

Further studies of mixtures have been inaugurated in this laboratory with a view of adapting them in special fields of surgery and treatment of the more elusive nervous and mental disturbances.

Tests on Lubricating Oils

The chemical engineering and the agricultural engineering departments of the A. and M. College of Texas have started an experiment to determine the properties of asphaltic base and paraffin base lubricating oils and the qualities that recommend them for use as lubricating oils in internal combustion engines. Several oil manufacturers have contributed samples of their products for experimental material, specimen automobile and tractor motors of different makes and types have been obtained from manufacturers, and the various kinds of oil will be subjected to a practical test in these engines. Before and after the oils are used the chemical engineering department will make various tests to ascertain the physical and chemical qualities, and to determine the relation between the laboratory tests and the actual value of the oil.

Manufacture of Research Chemicals at the University of Wisconsin

A summer course in the manufacture of organic chemicals is to be given at the University of Wisconsin under the direction of Prof. Glenn S. Skinner. It is planned to utilize the laboratory facilities for the manufacture of such chemicals as are needed in the various departments, and the staff have been asked to hand in their orders for chemicals.

Eight of the most promising advanced students will be admitted to the course. They will work from nine to ten hours a day, and will receive pay of about 40 cents an hour. The course offers an opportunity for intensive training in practical organic chemistry and experience in large-scale manipulation.

Sugar Production in the Philippines, 1920 to 1921

The sugar crop in the Philippine Islands for the season 1920-21 as estimated by the Philippine Bureau of Agriculture is 552,027 metric tons, an increase of 128,500 tons or 30 per cent over the previous season.

¹ Loc. cit.

Boron in Relation to the Fertilizer Industry¹

By J. E. Breckenridge

AMERICAN AGRICULTURAL CHEMICAL CO., CARTERET, N. J.

Owing to the lack of potash during the war, it was produced from many new sources, among which were materials which contained boron. In some parts of the country unusual agricultural conditions developed. Investigation revealed the fact that, in some cases, boron was present in fertilizers where injury to crops had occurred.

We find recorded experiments² showing stimulating effects with boron in small amounts and toxic effects when larger amounts are used.

The author's attention was called to a case in North Carolina where the farmer believed boron had injured his crop. On thorough investigation and analysis of the fertilizer used, the control officials reported boron absent. Again, another case came to the author's attention where an experienced farmer lost his crop of potatoes, but here again no boron could be found in the fertilizer used. These instances are mentioned to show that boron is not the only cause of trouble, and conclusions must not be drawn until a complete and thorough investigation has been made.

Injury to corn was first reported in Indiana in 1917.³ Later, trouble seemed to develop in the potato crop in Maine, and the tobacco and cotton crops in the South.

The Indiana Station⁴ and the U. S. Department of Agriculture⁵ carried on investigations, as well as the South Carolina Experiment Station.

The conclusions as to toxic limits which have been reached have been rather indefinite. The toxic effect of boron is dependent upon how the fertilizer or fertilizer material is applied, whether broadcasted or applied in the row, and whether or not there is a good rainfall soon after planting.

A series of experiments was conducted in the greenhouse under the writer's direction, with potatoes, beans, and corn.

POTATOES

A 4-8-4 fertilizer was made in the laboratory. The government quantitative method showed 0.01 per cent borax and the qualitative method showed less than 0.01 per cent.⁶ The fertilizer was used at a rate of 2000 lbs. per acre, in each pot, and spread out as evenly as possible, placing it approximately 2 to 3 in. under the seed.

Ten pots were used and the quantity of borax was as follows:

Lbs. per Acre
None (control)
4
6
8
10

¹ Presented before the Fertilizer Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

² Brenchley, "Inorganic Plant Poisons and Stimulants," University Press, Cambridge.

³ Purdue University, *Bulletin* 215.

⁴ *Bulletin* 239.

⁵ *Circular* 84.

⁶ Borax, whenever stated quantitatively, means anhydrous borax.

Good root growth was observed in the control pots and in the pots receiving 4 and 6 lbs. of borax per acre. The 8- and 10-lb. borax applications showed that the roots kept away from the fertilizer layer and developed near the surface of the soil.

The potato plants did not suffer very much, but this fact was probably due to the favorable condition which could not readily be duplicated in the field.

BEANS

Three treatments were made, using 4-8-4 fertilizer alone and with borax in the following quantities:

Lbs. per Acre
None (control)
6
10

In this case a marked injurious effect was early noticeable on the plants in borax-containing pots. The control plants grew very rapidly and the leaves were of a dark green, healthy appearance. The others showed the characteristic "gilt-edge" effect of borax; the leaves soon became spotted with yellow, which spread, and the leaves later dropped off. Growth, in both cases, as compared to that of the control, was stunted. The roots of the plants showed the effect of the borax, the control plants having all roots at the seed and going down into the fertilizer. The plants in the 6-lb. per acre application had poor seed roots and had a few at the surface.

The beans showed an even more marked recovery than in the case of potatoes. New leaves forming had a healthier appearance and were not so badly spotted.

CORN

The fertilizer used was 2-8-2, 2000 lbs. to the acre, and contained less than 0.01 per cent borax. Three treatments were made:

Lbs. per Acre
None (control)
6
10

The plants grew very slowly, and for about 3 wks. the tips of the plants having 6 and 10 lbs. of borax per acre became dry, and the edges of the leaves were slightly bleached. The plants partially recovered, however, and began to grow rapidly. The plants having no borax showed good seed root formation; the 6 lbs. of borax per acre, less seed roots and more surface roots; and the 10 lbs. borax per acre, still less seed roots and more surface roots.

CONCLUSIONS FROM THE POT EXPERIMENTS

1—From the experiments it is evident that certain percentages of borax are detrimental to plant growth, but under favorable conditions such as optimum moisture, good drainage, etc., rapid recovery is noticeable.

2—Corn and beans showed borax poisoning with 6 lbs. of borax per acre, and 10 lbs. per acre showed decided harmful results.

3—Potatoes showed no harmful effects, but rather stimulating, when 4 lbs. borax and even 6 lbs. borax

were used; 8 lbs. and 10 lbs. borax seemed to cause less root formation at the seed and more surface roots.

4—With optimum moisture plants seem to recover somewhat from the toxic effect of borax when used 6 lbs. per acre, but in short seasons the recovery would be too late for good crop results.

5—The fact that the fertilizer having more than 6 lbs. of borax to the acre prevented seed roots and the root system was largely near the surface, would result in the plants being stunted and probably dying in a dry season.

METHODS FOR DETERMINATION OF BORON

Much work has been done on the distillation method and the government method, both qualitative and quantitative, for determining boron.¹

ANALYST	SAMPLE										Blanks	
	G.	D.	G.	D.	G.	D.	G.	D.	G.	D.	Cc. 0.1 N NaOH	D.
1	0.25	0.27	0.17	0.13	0.11	0.10	0.09	0.09	0.05	0.04	0.4	0.07
2	0.25	0.25	0.10	0.13	0.07	0.09	0.08	0.07	0.02	0.05	0.15	..
3	0.25	0.33	0.16	0.20	0.08	0.13	0.14	0.12	0.07	0.09	0.4	1.0
4	0.19	0.18	0.11	0.13	0.09	0.08	0.07	0.08	0.04	0.06	0.00	1.20
5	0.27	0.29	0.15	0.16	0.13	0.09	0.06	0.05	0.08	0.03	0.4	0.4
6	0.19	0.22	E..	..	0.16	0.12	E..	..	0.08	0.04	E..	..
	..	0.20	0.10	0.05	0.9	0.3
7	0.26	0.10	0.05	..	0.2	..
8	0.21	L..	0.07	L..	0.04	L..	0.12	..
9	0.21	0.08	0.01
10	RT	RD	RT	RT
	0.40	0.32	0.07	0.02
11	(0.05)	0.01	Plus Q..	0.01	Plus Q..
(Plus Q.)	0.22	0.20	0.08	0.07	0.03	0.03	0.35	0.35

E—Evaporating distillate to dryness and proceeding as in determining salts.

L—Lipscomb method—Clemson College, S. C.

RT—Results by turmeric method according to Rudnick.

RD—Distillation method according to Rudnick.

Q—More than—by qualitative turmeric test—Swift.

G—Government method—Bureau of Soils.

D—Gladding method—distil with methanol.

Other methods have been suggested, but are, as a rule, modifications of these two. Jones and Anderson¹ of the Vermont Station have suggested a modification which is accurate and speedy. The South Carolina Experiment Station has proposed a method worked out by Lipscomb, Inman and Watkins.²

Five samples of varying percentages of borax were prepared by the writer and analyzed by five different chemists, and three of the samples were analyzed by eleven different chemists. The results are given in the accompanying table.

The borax content in Sample 1 was 0.25 per cent, and in Sample 5 less than 0.01 per cent. The other samples were:

Sample 2—0.5 No. 1 and 0.5 No. 5

Sample 4—0.25 No. 1 and 0.75 No. 5

Sample 3—0.33 No. 1 and 0.66 No. 5

Since this work has been done everyone has had more experience with the borax determinations, and the results as listed under Sample 5, which show from 0.01 up to 0.08 per cent by the government method, have been reduced to 0.01 per cent and less.

CONCLUSIONS

The government method gives accurate results when carefully carried out, but time may be saved by using the Jones and Anderson modification.

All reagents must be free from carbonate.

Separation of the phosphates must be complete and no precipitate should form on standing after the final titration, which point is noted in the government method.

Results should be confirmed by the qualitative test.

Determination of Chlorides in Petroleum²

By Ralph R. Matthews

ROXANA PETROLEUM CORPORATION, WOOD RIVER, ILLINOIS

In order to determine the corrosiveness of water in petroleum, and the amount of soluble salts which may be crystallized and precipitated when the oil is distilled, a determination of chlorides in the water is generally necessary. Some light petroleum easily give up this water, and a sample can be obtained and readily titrated. There are oils, however, which do not become entirely anhydrous no matter how long they are allowed to settle, though they may eventually reach a point where there is 0.2 to 0.4 per cent of water and sediment. For such oils the method described below has been evolved so that a determination of the chlorides may be easily possible. Various other methods than the one shown have also been tried, but have failed to give concordant results.

OUTLINE OF METHOD

The sample of oil is thoroughly mixed by shaking the can, or other receptacle, in which it has been received, so that whatever salt water is present may be uniformly distributed in the oil, and 500 cc. are carefully measured into a 500-cc. graduated cylinder. The oil is then drained into a 2000-cc. graduated, glass-stoppered cylinder, and 125 cc. of acetone are mea-

sured in the same 500-cc. cylinder. (The U. S. P. grade of acetone may be used, but it must be tested to be sure no chlorides are present.) After the acetone has been added to the oil in the 2000-cc. cylinder, the two are thoroughly mixed by shaking for approximately 3 min. The action of the acetone appears to be two-fold, to reduce the viscosity of the oil, and to take up and collect the salt water. The total volume is now brought up to 2000 cc. with 1375 cc. of distilled water, which is also measured in the 500-cc. cylinder, thus thoroughly cleaning out all chlorides which may have been left in the cylinder. The distilled water, oil, and acetone should be completely mixed for approximately 5 min. Care must be taken in shaking, since too violent an agitation has a tendency to produce a semi-emulsion which will settle out quite slowly. This is especially true of oil which contains much paraffin, and extreme agitation has not been found necessary for complete extraction of the acetone and salt water. The contents of the cylinder are allowed to settle until approximately 500 cc. of the water and acetone have settled out. About 400 cc. of the acetone-water mixture are next drawn off with a glass siphon. If a lit-

¹ *Am. Fertilizer*, March 13, 1920.

² Received January 20, 1921.

¹ *Am. Fertilizer*, April 10, 1920.

² *Ibid.*, February 28, 1920.

the oil comes with it, it is removed by filtering through dry filter paper. An aliquot part, depending on the salt content, is then concentrated for titration with a solution of approximately 0.05 *N* silver nitrate, using potassium chromate as an indicator. From these results the chlorine can be calculated, or, if previous analysis of similar brine has shown it to consist mostly of sodium chloride, it may be calculated as such.

We have tested the accuracy of the method by making a re-treatment of some of the oil which had settled out after the treatment outlined above. A mere trace of chlorides could be found, thus furnishing good proof that the first treatment had effected their almost complete removal.

The method has been used for about a year, and the following check results, expressed as grams of salt per liter of oil, have been obtained:

Gravity of Crude ° B _e	B. S. & W. Per cent	Water by Dist. Per cent	First Result G.	Second Result G.
30.9	1.0	0.8	0.77	0.75
36.5	2.2	1.6	0.49	0.50
31.3	0.6	0.5	0.72	0.75
35.8	0.9	0.8	0.35	0.37
32.3	1.6	1.1	0.60	0.59
31.4	0.8	0.6	0.67	0.68

ACKNOWLEDGMENT

Experimental work on the method was carried out in this laboratory by Messrs. Philip A. Crosby and John G. Campbell.

LABORATORY AND PLANT

Humidity Control by Means of Sulfuric Acid Solutions, with Critical Compilation of Vapor Pressure Data¹

By Robert E. Wilson

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

NEED FOR HUMIDITY CONTROL IN LABORATORY WORK

In the course of both research and routine laboratory work, many occasions arise when it is desired to maintain a definite humidity in an enclosed space or to produce a stream of air of definite moisture content. In studying the humidity equilibria and rate of drying of various substances, such control is, of course, a prime requisite. There are, however, many other properties of materials which vary greatly with changes in their moisture content. In order to obtain reproducible results in any investigation which relies upon the quantitative measurement of such properties, it is therefore necessary either to test the materials in an atmosphere of a definite humidity, or else, when the time of the test is short compared with the rate of taking up moisture, previously to equilibrate them with a definite humidity.

In cases where only a single humidity is to be used for such tests, this Laboratory has adopted 50 per cent relative humidity as a standard for articles which are to be tested under conditions approximating those prevailing indoors, and 65 per cent humidity to approximate those prevailing outdoors. In many cases, however, it is necessary to make the tests under a variety of conditions. Accurate control of temperature is generally not as important as control of humidity, as the moisture content of most materials varies but little with moderate changes in temperature, providing the relative (not absolute) humidity is kept constant.

The object of this article is not to suggest any new methods of obtaining this humidity control, but merely to present in convenient form the data which this laboratory has compiled from the literature, or found by practical experience, with reference to what seems to be the most satisfactory method of small-scale humidification, namely, the use of sulfuric acid solutions of definite composition.

ADVANTAGES OF SULFURIC ACID SOLUTIONS FOR HUMIDITY CONTROL

Sulfuric acid solutions have many advantages over other materials which might conceivably be used for this purpose. Homogeneous solutions varying from 0 to 100 per cent water can be obtained; the vapor pressure of these solutions has been much more accurately determined than for any other concentrated solutions; the composition, and hence the vapor pressure, of the solutions can be quickly and accurately determined by measuring their density, which varies greatly with changes in composition; their relative vapor pressure (per cent of that of pure water at the same temperature) varies but little with wide changes in temperature; they come to equilibrium rapidly with the surrounding atmosphere; the sulfuric acid itself exerts no appreciable vapor pressure; and finally, material of adequate purity is cheap and readily obtainable.

For the purpose of maintaining a constant humidity in a closed chamber, sulfuric acid solutions have no real competitor under ordinary conditions, since it is merely necessary to place within the chamber some acid of the proper strength with an amount of surface exposed in general somewhat larger than that of any other moist or hygroscopic material present.

When a fairly large stream of humidified air is to be produced it is, of course, possible to obtain it by mixing two streams of air, one of which has been thoroughly dried and one of which has been bubbled through water. By varying the relative amount of the two streams it is possible to obtain any desired humidity. This necessitates, however, both drying and humidifying fairly large amounts of air, and also the maintenance of an absolutely constant ratio between the two streams. It also requires frequent analytical control which, at lower temperatures, necessitates the use of an absorption method. At higher temperatures wet and dry bulb thermometers

¹ Received December 14, 1920.

may be employed to determine the humidity, but this method necessitates the rejection of that fraction of the air which passes over the wet bulb and thereby picks up an uncertain amount of additional moisture. Under ordinary conditions in the laboratory this method is much more cumbersome and expensive than the simple procedure of bubbling the stream through sulfuric acid of a definite composition. The former method does, however, find some application under certain exceptional conditions where fairly high humidities are to be produced and there is available an air supply of reasonably constant low humidity which does not require chemical desiccation.

Since the sulfuric acid method has thus been shown to be remarkably well adapted for all-round purposes as a laboratory method of humidification, this Laboratory has made a careful study and compilation of the best available data on the vapor pressure and density of sulfuric acid solutions as dependent upon their composition and temperature.

COMPILATION OF VAPOR PRESSURE DATA

The first step in compiling the vapor pressure data was to plot on a large scale the results of four investigators¹ who have determined the vapor pressure at 25° C. of sulfuric acid solutions as a function of their concentration. These results showed a surprisingly good concordance throughout the middle range of concentrations (30 to 60 per cent H_2SO_4 , or 17 to 76 per cent relative humidity), but somewhat larger deviations at the two extremes. It therefore appeared desirable to make use of the very careful work of Dieterici,² who unfortunately made his measurements at 0° C. It is possible, however, by a simple and surprisingly accurate thermodynamical calculation (made as described hereinafter) to convert these results over to the corresponding values for 25° C. The addition of this series of points left little doubt as to the precise location of the curve except in the range between 65 and 85 per cent H_2SO_4 . The uncertainty in this region might be expected on account of the very low vapor pressures exerted by such solutions at 25° C. (0.2 to 2.3 mm.), and especially at 0° C., which makes their accurate measurement extremely difficult.

At higher temperatures, however, these vapor pressures become quite large and can be measured readily and accurately. Fortunately, three investigators have determined the vapor pressure of such concentrated solutions at temperatures of 75° or 100° C., and their data were also calculated to 25° C. by similar thermodynamical calculations.

When these results were compared with those measured at 25° C., it appeared quite certain that Sorel's low temperature results were somewhat too high in this range, while those of Regnault and Bronsted were more nearly correct. This is not surprising in view of the fact that if Sorel's original data in the low temperature-high concentration range are plotted, the points vary widely from a smooth curve, and do

not correspond with his own figures obtained at higher temperatures, when they are calculated over by thermodynamical methods.

It is thus possible to draw a vapor pressure-composition curve for sulfuric acid solutions at 25° C. (see heavy line, Fig. 1) which is probably accurate within 0.1 mm. throughout. It will be noted that *relative* vapor pressures (per cent of that of pure water at the same temperature, thus corresponding to the *relative* humidity of the air) are plotted rather than the *absolute* values in millimeters, because the former vary but little with temperature, and also because they are more significant for most laboratory purposes. The absolute vapor pressures at any temperature can readily be calculated by reference to steam tables or other sources of vapor pressure data for pure water.

The encircled points in Fig. 1 all correspond to actual measurements at 25° C., while those in triangles are points calculated to 25° from measurements made at other temperatures. Table I presents the original observed values and those calculated over to 25° C. for all the latter group of points.

TABLE I—CALCULATED VALUES FOR RELATIVE VAPOR PRESSURE OF DILUTE SULFURIC ACID AT 25° C.

INVESTIGATOR	H_2SO_4 Per cent	Temp. t° C.	Vapor Pressure Mm.	Relative Vapor Pressure at t° C.	Calculated Relative Vapor Pressure at 25° C.
Dieterici.....	5.62	0	4.535	98.0	98.1
Dieterici.....	9.24	0	4.452	96.4	96.6
Dieterici.....	15.73	0	4.284	92.7	93.1
Dieterici.....	20.8	0	4.065	87.9	88.6
Dieterici.....	27.2	0	3.664	79.3	80.3
Dieterici.....	32.8	0	3.200	69.3	71.2
Dieterici.....	35.4	0	2.952	63.9	66.2
Dieterici.....	40.5	0	2.435	52.7	55.2
Dieterici.....	47.3	0	1.748	37.8	40.8
Dieterici.....	53.4	0	1.206	26.1	29.1
Dieterici.....	61.3	0	0.569	12.3	14.7
Burt.....	62.8	75	45.9	15.9	11.6
Dieterici.....	68.5	0	0.164	3.5	4.6
Burt.....	70.8	100	57.0	7.5	3.7
Sorel.....	74.0	75	12.1	4.2	2.3
Briggs.....	77.5	100	20.2	2.66	0.94
Briggs.....	78.0	75	7.0	2.4	1.14
Briggs.....	79.2	100	14.3	1.88	0.61

Again using thermodynamical methods, it is possible to calculate, from the accurately located 25° C. curve, similar curves for other temperatures at which little or no direct experimental data are available. Such curves (dotted) are also shown in Fig. 1 for 0°, 50°, and 75° C. By means of these curves it is possible to determine readily and accurately the vapor pressure of any sulfuric acid solution at any temperature between 0° and 100° C. In order to make possible the reproduction of these curves on a large-scale plot, a series of points are presented in Table II.

TABLE II—BEST VALUES FROM VAPOR PRESSURE CURVES FOR SULFURIC ACID SOLUTIONS

H_2SO_4 Per cent	Relative Vapor Pressure 0° C.	Relative Vapor Pressure 25° C.	Relative Vapor Pressure 50° C.	Relative Vapor Pressure 75° C.
0	100.0	100.0	100.0	100.0
5	98.4	98.5	98.5	98.6
10	95.9	96.1	96.3	96.5
15	92.4	92.9	93.4	93.8
20	87.8	88.5	89.3	90.0
25	81.7	82.9	84.0	85.0
30	73.8	75.6	77.2	78.6
35	64.6	66.8	68.9	70.8
40	54.2	56.8	59.3	61.6
45	44.0	46.8	49.5	52.0
50	33.6	36.8	39.9	42.8
55	23.5	26.8	30.0	33.0
60	14.6	17.2	20.0	22.8
65	7.8	9.8	12.0	14.2
70	3.9	5.2	6.7	8.3
75	1.6	2.3	3.2	4.4
80	0.5	0.8	1.2	1.8

It will be noted that for a temperature change of 5° or 10° C. the relative vapor pressure of most of the

¹ Regnault, *Ann. chim. phys.*, [3] 15 (1845), 179; Sorel, *Z. angew. Chem.*, 1889, 272; Helmholtz, *Wied. Ann.*, 27 (1886), 532; Bronsted, *Z. physik. Chem.*, 68 (1909), 693.

² Dieterici, *Wied. Ann.*, 50 (1893), 60; 62 (1897), 616.

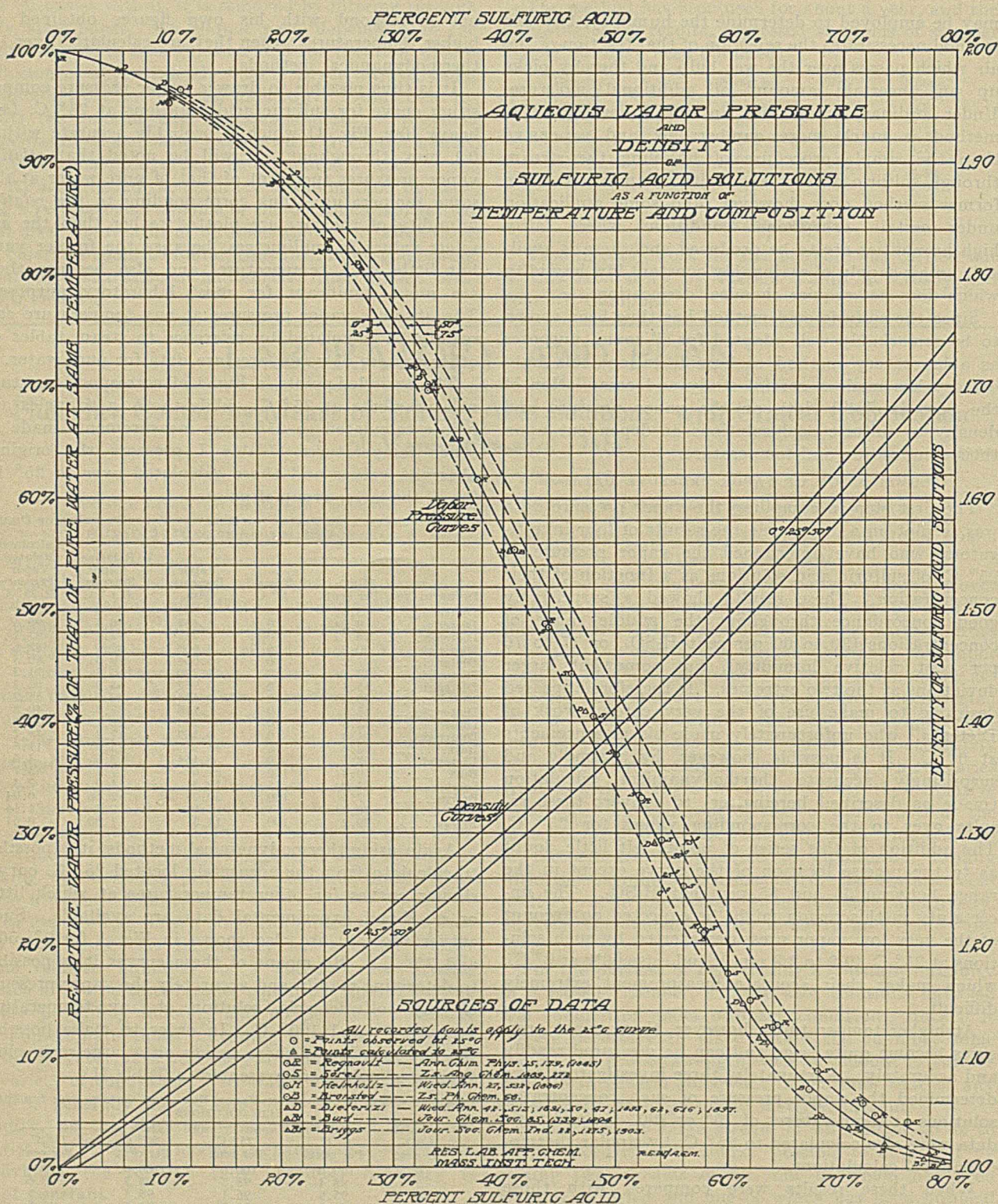


FIG. 1

solutions is practically constant; furthermore, the small increase which does occur with increasing temperature is in the right direction to compensate for a similar slight tendency on the part of practically all materials whose humidity equilibria have been determined.¹ It is therefore not necessary when study-

¹ It is planned in the near future to present values which have been determined by this laboratory and others for the humidity equilibria of various substances, such as wood, paper, cotton, silk, wool, jute, leather, rubber, carbon black, etc.

ing such equilibria to attempt to maintain the system at a temperature any more constant than that of the average laboratory.

The information most frequently desired, however, is not what vapor pressure is exerted by a solution of given concentration, but what concentration of acid should be used to obtain a given vapor pressure. This information is conveyed in Table III, which is also determined from Fig. 1 drawn on a large scale.

TABLE III—STRENGTH OF H_2SO_4 REQUIRED TO GIVE DEFINITE HUMIDITIES

Relative Humidity Per cent	0° C.	25° C.	50° C.	75° C.
10	63.1	64.8	66.6	68.3
25	54.3	55.9	57.5	59.0
35	49.4	50.9	52.5	54.0
50	42.1	43.4	44.8	46.2
65	34.8	36.0	37.1	38.3
75	29.4	30.4	31.4	32.4
90	17.8	18.5	19.2	20.0

PRACTICAL USE OF THE VAPOR PRESSURE CHART

Since density determinations afford a very satisfactory and rapid method of determining the exact concentration of sulfuric acid solutions, Fig. 1 also includes curves showing the variations in this property with temperature and concentration. These are constructed from the very accurate data of Domke.¹

To prepare a solution having a specified vapor pressure at a given temperature, it is therefore only necessary to refer to Fig. 1 to find the proper concentration of acid, and also the density of the solution. The temperature at which the density is determined need not be that at which the solution is to be used, providing the proper curves are used. Thus the density curves in Fig. 1 indicate that in order to obtain a relative humidity of 50 per cent at 25° C., 43.4 per cent H_2SO_4 should be used, and this acid has a density of 1.329 at the same temperature. If, however, it be desired to determine the concentration before the solution has had time to cool after pouring the strong acid into the water, another line shows that the density of the acid at 50° C. is 1.311. It is unwise to attempt to measure densities at temperatures higher than this, but the values for intermediate temperatures can readily be determined by interpolation.

Either vapor pressure or density values at any temperature between 0° and 100° C. can readily be obtained by a simple inter- or extrapolation. Sufficiently accurate density determinations can be made by any properly calibrated (water at 4° C. = 1) Westphal balance or hydrometer reading to three decimal places, a pycnometer being more accurate than is necessary.

RECOMMENDED METHODS OF DETERMINING HUMIDITY EQUILIBRIA

In determining the humidity equilibrium of any substance at a given temperature, the most satisfactory general method is to subdivide it until the amount of surface exposed is reasonably large, place from 20 to 60 g. in a small straight or U-tube of known weight, and pass a slow stream (50 to 500 cc. per min., using the higher rates at lower temperatures) of properly humidified air through it. In no case should any glass wool or cotton be used in the tubes. The tube containing the material is weighed every few hours until constant weight is reached, after which the moisture content may be determined, preferably by passing through it a stream of warm air (50° to 125° C., depending on the nature of the material) previously dried by P_2O_5 , until constant weight is reached. The loss in weight, of course, represents the equilibrium moisture content at the temperature and

humidity in question. In order to make certain that substantial equilibrium has been reached, in any given case, it is always desirable to approach it from both the dry and the moist sides.¹ The simplest way to accomplish this and to determine all the points on the curve with a single sample is to pass fairly dry air through at the start, and then determine in turn the equilibrium weights at 10, 25, 50, 75, and 90 per cent humidity; saturated air is then passed through for a short time and the same points redetermined in the reverse order, finally obtaining dry weight at the elevated temperature. Moisture contents should preferably be expressed as per cent of the dry weight.

In general, equilibrium can be reached from 18 to 96 hrs., and the dry weight within 2 to 6 hrs., depending largely on the state of subdivision of the material. Higher water contents and lower temperatures require the longer times. These rates are much more rapid than can be obtained by the frequently used method of exposing the sample over sulfuric acid, where the rate of approaching equilibrium has been found to be surprisingly slow, due to the slow rate of diffusion in still air. If a small fan be used in the desiccator, and a stirrer in the acid, the rate can be made to approach that of the tube method, but this is difficult to arrange in an ordinary desiccator. The use of vacuum greatly increases the rate of approaching equilibrium, but is quite likely to introduce errors on account of the inrush of unconditioned air when the vacuum is broken preparatory to removing and weighing the exposed sample.

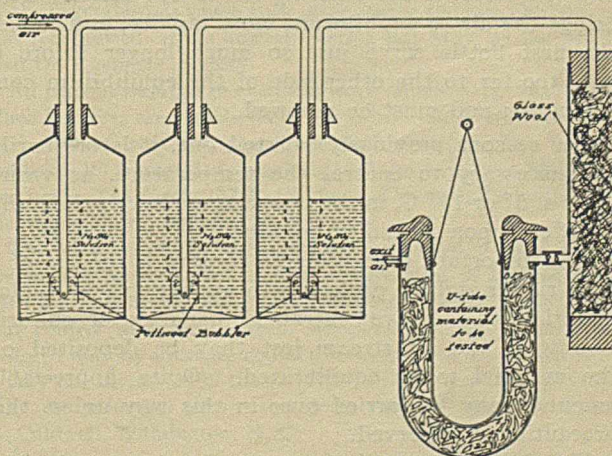


FIG. 2—APPARATUS FOR DETERMINING HUMIDITY EQUILIBRIA

A few precautions must be observed in conditioning the air stream. If the rate of flow is more than about 100 cc. per min., some special form of bubbler, designed to give good contact between liquid and gas, should be employed. A petticoat type such as that indicated in Fig. 2 has been found to give excellent results. The use of broken glass or beads in the acid bottle also aids in distorting or breaking up the bubbles

¹ While the two figures thus obtained will generally agree within narrow limits, some colloidal materials which tend to be highly hydrated or form gels will exhibit different apparent equilibrium values, depending on the side from which it is approached. This appears to be due to a hysteresis effect frequently observed in such materials, which may require a matter of months or years to reach substantially the same structure when approaching the same point from opposite sides.

¹ Z. physik. Chem., 43 (1905), 125; also Landolt-Börnstein, 1912, 265.

of air and bringing them to equilibrium. With such bubblers, substantial equilibrium can ordinarily be reached, even with only two bottles in series, at rates of flow up to 2 liters per min.

In case the entering air is very far from the desired humidity, or if the rate of flow is rather high (2 to 10 liters per min.), three bottles should be used in series. If for any reason it is desired to humidify larger amounts than this, either two parallel lines of bubblers or a tower filled with glass beads, over which acid is trickling, should be used. The recommended size of the acid bottles varies from about 500 cc. for the slower rates of flow to 2 liters for the higher. They should be filled about half full of acid.

In order to determine when the acid needs to be replaced, it has been found desirable to mark the initial level of acid in each humidity bottle. If three bottles are used, as is recommended for most purposes, the volume of acid in the first bottle can be allowed to change by 3 or 4 per cent before it is necessary to add water or acid to restore the original concentration. The density of the acid in the second and third bottles should be checked up occasionally, but will usually be found to change but little if the concentration in the first bottle is properly adjusted. If the humidity of the entering air is known to be considerably lower than the desired value it is generally desirable to have the *initial* water content of the *first* bottle 2 or 3 per cent higher than the true equilibrium concentration used in the last two bottles, and *vice versa*, if the entering air is too moist. This brings the air to equilibrium more rapidly, and makes the first bottle serve just so much longer before it goes too far to the other side of the equilibrium concentration and must be renewed.

For reasons previously pointed out, it is ordinarily not necessary to control the temperature, as variations of 5° or 10° C. in the temperature have practically no effect upon humidity equilibria.

One important precaution to observe is the use of a tube rather tightly packed with glass wool, or similar material, to remove entrained particles of sulfuric acid from the air stream lest they be deposited on the material to be equilibrated. Quite appreciable amounts may be carried over in this way unless this precaution is observed.

Fig. 2 shows a typical set-up of apparatus for the rapid and accurate determination of the humidity equilibrium of a fibrous material such as cotton.

METHOD OF CALCULATING TEMPERATURE CORRECTIONS

Since it might be desired to extend the foregoing data over still wider temperature ranges, probably with some sacrifice of accuracy, it appears desirable to present as briefly as possible the method of calculating the vapor pressure values from one temperature to another, together with the thermochemical data on sulfuric acid solutions which was assembled for the purpose.

The basis of the calculations was, of course, the approximate form of the Clausius-Clapeyron equation, *viz.*,

$$\frac{d \ln p_s}{dT} = \frac{\Delta H}{RT^2} = \frac{\Delta H_1 + \Delta H_2}{RT^2},$$

where ΔH is the heat absorbed in the evaporation of one mole of water from a large amount of the solution (so that there is no appreciable change in concentration). This is equal to the sum of the heat effects involved in removing one mole of liquid water from the solution and in evaporating it, or to $\Delta H_1 + \Delta H_2$; where ΔH_1 is the molal heat of vaporization of pure water and ΔH_2 is the heat absorbed when one mole of water is removed from solution without change in concentration.

Since the same equation applies to pure water, *viz.*,

$$\frac{d \ln p_w}{dT} = \frac{\Delta H_1}{RT^2}$$

it is possible to eliminate the large quantity, ΔH_1 , by subtracting the second equation from the first, and thus obtain a very accurate expression for the ratio p_s to p_w , which will be called r , the *relative* vapor pressure of the solution, as previously defined. This expression,

$$\frac{d \ln r}{dT} = \frac{\Delta H_2}{RT^2}$$

can be integrated on the assumption that ΔH_2 is independent of the temperature,¹ giving the equation used in the calculations, namely,

$$\log \frac{r_2}{r_1} = \frac{\Delta H_2}{2.3 R} \cdot \frac{T_2 - T_1}{T_2 T_1}.$$

To obtain the values of ΔH_2 for different concentrations, use was made of the data of Bronsted² on the heat of dilution of sulfuric acid, apparently at 18° C. These appear to be better than the earlier data of Thomson, who probably had a small amount of water in his supposedly pure sulfuric acid. Bronsted gives values of Q (total heat of dilution) for the reaction



where n varies from 0 to 15.

In order to obtain similar values of Q for other temperatures it is necessary to make use of Kopp's Law,

$$\frac{dQ}{dT} = \Sigma \Gamma_1 - \Sigma \Gamma_2,$$

where $\Sigma \Gamma_1$ and $\Sigma \Gamma_2$ are the heat capacities of the reacting materials and the reaction products, respectively. In comparing the results of various investigators on the heat capacities of sulfuric acid solutions, especially Thomson,³ Berthelot,⁴ Marignac,⁵ Cattaneo,⁶ Pickering,⁷ and Schlesinger,⁸ the agreement was not found to be highly satisfactory. Fortunately, however, the specific heats are mere minor correction terms for the purpose in hand, and need not be known with great accuracy. The values used were taken

¹ This involves no appreciable error since, as noted later, the value used for ΔH_2 was always that for the mean between the particular T_1 and T_2 in question.

² *Z. physik. Chem.*, **68** (1909), 693.

³ *Pogg. Ann.*, [3] **30** (1853), 261; also "Thermochemische Untersuchung," **3**, 1.

⁴ *Ann. chim. phys.*, [5] **4** (1875), 446.

⁵ *Arch. Soc. Phys.*, **39** (1870), 217; **55** (1876), 113.

⁶ *Nuovo Cimento*, [3] **26** (1889), 50.

⁷ *J. Chem. Soc.*, **57** (1890), 91.

⁸ *Physik. Z.*, **10** (1909), 210.

from a smooth curve which appeared to be representative of the more recent and better work, and which may be reproduced from Table IV.

TABLE IV—VALUES ASSUMED FOR SPECIFIC HEATS OF SULFURIC ACID SOLUTIONS AT 18° C.

Per cent H ₂ SO ₄	Specific Heat
0	1.00
20	0.84
40	0.68
60	0.53
80	0.41
100	0.34

Using these data, the corresponding values of Q at the desired mean temperatures were calculated and the results are presented in Table V.

TABLE V—CALCULATED HEATS OF DILUTION (Q) OF ADDING n H₂O TO 1 H₂SO₄ AT DIFFERENT TEMPERATURES (In Calories per Mole of H₂SO₄)

n	Per cent H ₂ SO ₄	18° (obs.)	12.5°	37.5°	50°	62.5°
1	84.5	6,710	6,680	6,830	6,900	6,980
1.5	78.4	8,790	8,750	8,940	9,040	9,140
2	73.1	10,020	9,970	10,190	10,300	10,400
3	64.5	11,640	11,570	11,880	12,040	12,200
4	57.7	12,830	12,760	13,090	13,250	13,420
7	43.8	14,890	14,820	15,160	15,330	15,500
9	37.7	15,620	15,540	15,890	16,060	16,230
15	26.6	16,660	16,580	16,950	17,130	17,320
19	22.3	16,990	16,900	17,290	17,480	17,680
a			18,090	18,600	18,870	19,110
b			1.646	1.666	1.676	1.684

The amount of heat evolved (ΔH_2) when one mole of water is added to a large amount of a solution of a definite concentration is of course equal to the rate at which the total heat of dilution, Q , is changing at that particular concentration. This may be determined by plotting Q against n and determining by graphical methods the slope of the tangent (ΔH_2) at a given concentration. It was found more accurate and convenient, however, to perform this operation analytically. Thompson had shown that the heat of dilution of sulfuric acid could be expressed fairly accurately by an equation of the form

$$Q = \frac{an}{n+b}$$

In order to determine the value of the coefficients a and b , it is only necessary to substitute two values of n and Q and solve the two equations simultaneously.¹ Having obtained the equation of the curve, the values of ΔH_2 were readily and accurately calculated by taking the first derivative for the proper values of n , i. e.,

$$\Delta H_2 = \frac{dQ}{dn} = \frac{a}{n+b} - \frac{an}{(n+b)^2}$$

Tables VI and VII present values of ΔH_2 and of $r_2 : r_1$ ratios calculated in this way for various percentages of sulfuric acid. Using these ratios it is obviously a simple matter to calculate an observed vapor pressure at any one of the indicated temperatures over to any other of these temperatures, or, by interpolation, to intermediate temperatures. Although these correction ratios appear large in the case of the more concentrated solutions, it should be remembered that the vapor pressures in these regions

¹ Actually, in order to distribute the inaccuracies over the curve, three pairs of values of n were taken, namely, 1 and 3, 1.5 and 4, and 2 and 7, and the three values of a and b averaged. Using these average values of the coefficients (see Table V), it was found that the maximum deviation of the calculated from the original observed values of Q was less than 150 cal. up to $n = 4$ and less than 300 from $n = 7$ on.

are very low, so that the error in calculating any vapor pressure from 25° to 75° C. certainly cannot exceed 0.4 per cent relative vapor pressure. The maximum probable error from all sources of any of the curves shown in Fig. 1 is about 0.6 per cent relative humidity.

TABLE VI—VALUES OF ΔH_2 FOR VARIOUS CONCENTRATIONS AND MEAN TEMPERATURES

Per cent H ₂ SO ₄	n	12.5°	37.5°	50°	62.5°
20	21.8	54	56	58	59
30	12.72	145	150	153	155
40	8.18	290	320	326	330
50	5.45	593	612	624	630
60	3.63	1068	1108	1128	1152
70	2.34	1870	1940	1962	1996
80	1.36	3290	3380	3430	3460

TABLE VII—FACTORS TO BE APPLIED TO RELATIVE VAPOR PRESSURE AT 25° TO GIVE RELATIVE VAPOR PRESSURE AT TEMPERATURES INDICATED

Per cent H ₂ SO ₄	0°	50°	75°	100°
20	0.992	1.007	1.014	1.020
30	0.978	1.020	1.038	1.054
40	0.956	1.043	1.082	1.116
50	0.912	1.084	1.163	1.236
60	0.848	1.156	1.314	1.478
70	0.749	1.289	1.608	(1.968)
80	0.601	1.556	(2.295)	(3.240)

ACKNOWLEDGMENT

The writer desires to express his appreciation of the assistance rendered by Dr. D. R. Merrill in making the thermodynamic calculations involved in the preparation of this article.

American Oil Chemists' Society

For a number of years the leading chemists of the cottonseed oil industry have been associated in the Society of Cotton Products Analysts. As a result of the widening of the field of the vegetable oils which took place during the war, the Society was reorganized at its annual meeting last May, as the American Oil Chemists' Society.

All persons engaged in chemical work on oils, fats, waxes, and allied interests are eligible for active membership, provided they have had at least five years' chemical training. The Society publishes its transactions regularly and maintains the Chemists' Section in *The Cotton Oil Press*, devoted exclusively to the edible vegetable oil industry.

The membership also includes those interested in the so-called technical aspects of the industry. Since most of the oils dealt with are industrially more or less interchangeable, their chemical control and technological development can be properly fostered only by intimate contact between science and industry.

Any one interested in the activities of the new organization may obtain further information from the secretary, Mr. Thos. B. Caldwell, Wilmington, N. C.

T. A. P. P. I. Meeting

The annual meeting of the Technical Association of the Pulp and Paper Industry is to be held at the Waldorf-Astoria and the Hotel Astor, New York City, April 11 to 14, 1921.

Engineering problems in the industry will be broadly considered in committee reports and in special papers. Among the subjects considered will be a new groundwood process, preliminary impregnation of wood as a means of shortening the cooking time in the sulfite process, the operation of water-power plants at maximum efficiency, the measurement of moisture in chips for cooking, the testing of crude rosin, methods of drying paper on paper machines, and the electrification of paper machinery. On Wednesday, April 13, a discussion, in charge of the committee on heat, light, and power, will be conducted on Pulverized Fuel and Steam Economy.

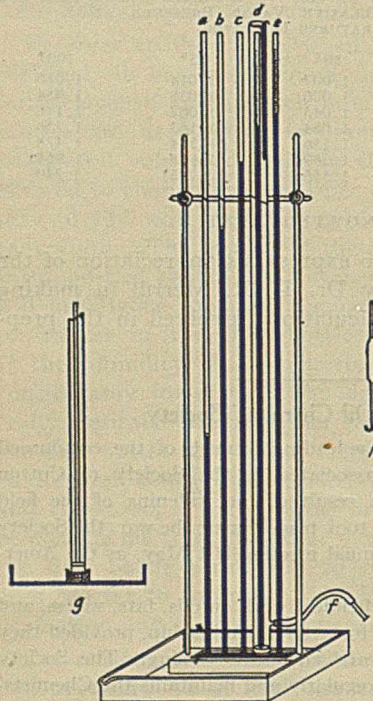
Notes on Laboratory and Demonstration Apparatus¹

By Clifford D. Carpenter

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

APPARATUS FOR DEMONSTRATING THE VAPOR PRESSURE OF LIQUIDS

The apparatus herein illustrated shows five Torricelli tubes standing in a special overflow trough. The principal feature is that the inner trough is small and uses little mercury, and the sides are low so that the mercury runs over into the outer trough when too full. This gives a constant zero point at the lower end of the tubes. The cross-section, *g*, gives the detail.



Two rods, each 3 ft. in length, are screwed into the ends of the inner trough and are used as supports for a crossbar by which the tubes are held in position. In practice a rubber band or cord is sufficient to hold the tubes in place against the crossbar. Tube *d* is fitted into a large stopper which closes the lower end of a large tube used as a jacket. This large open tube has an outlet, *f*, at its lower end, making it possible to change the water

and to surround *d* with water at definite temperatures. Tubes *d* and *e* are graduated in mm. from the bottom upward, making it possible to read the height of the mercury column directly.

In a demonstration all tubes are filled with mercury and inverted, and the heights of the columns noted. The jacket about *d* is filled with water at room temperature. By the aid of pipets, *h*, water is introduced into *d*, alcohol into *c*, chloroform into *b*, and ether into *a*, while *e* is left as a comparison tube. Attention may then be called to the relative vapor pressures of the different substances. If tubes *d* or *e* are not graduated a meter stick may be used. The depression of the mercury in *d* is measured and the temperature noted. Water of a different temperature is then introduced into the jacket around *d* and the depression and temperature again noted, and the results are compared with the aqueous tension tables given in the handbooks.

A RINGSTAND SET

Mobility of apparatus after it is assembled for use in an experiment is most desirable. This is especially

true in the case of a lecture demonstration, for if each experiment can be set out in some prominent place while under discussion, the pupils can follow the procedure much more readily than when the experiment is one of a long line arranged from one end of the desk

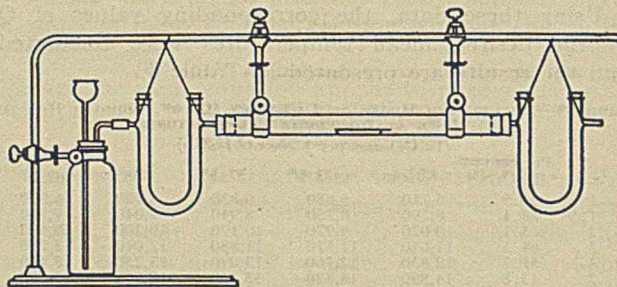


FIG. 1

to the other. A slight alteration in the common ringstand makes it possible to mount the apparatus used in many experiments, ordinarily requiring two or more supports, upon a single support. The illustrations in Figs. 1 and 2 show two simple alterations which have been found very practical and useful.

Such modifications would also prove very useful to students. Each student could be provided with a ringstand set as follows: a base 7 in. \times 10 in. and three interchangeable rods; a straight rod 26 in. \times 0.375 in. which, when mounted in the base, would give the ordinary ringstand; a second rod 36 in. \times 0.375 in. bent at right angles, so that when mounted in the base the horizontal portion is 11 in. above the base, as illustrated in Fig. 1; and a third rod 36 in. \times 0.375 in. bent so that the two portions make an angle of 75°, as illustrated in Fig. 2, so that when mounted the perpendicular portion is about 18 in. in length.

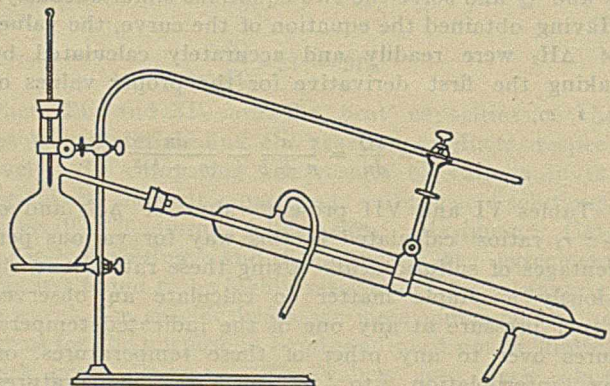


FIG. 2

While the rods may be screwed into the base it is not entirely satisfactory, as rusting and wear will gradually make the interchange of rods difficult. Moreover, the bent rods must always take the same position with respect to the base when mounted. This difficulty is easily overcome by using a "lock socket."

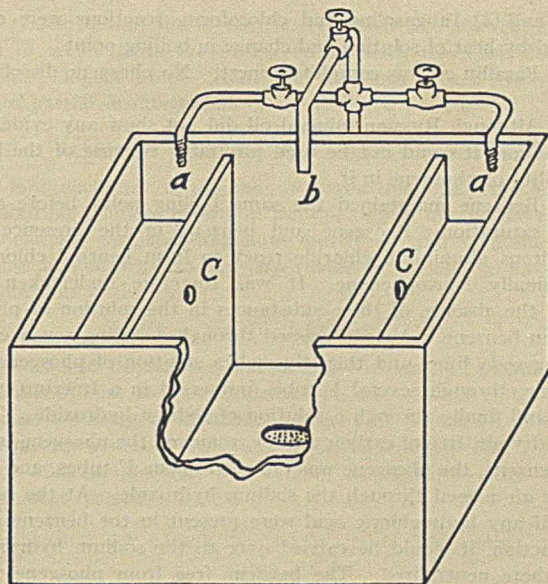
¹ Received December 7, 1920.

LABORATORY SINK

The accompanying sketch illustrates a convenient form of sink for laboratories in elementary and general chemistry. The main feature of the sink is its three compartments. The two smaller compartments drain into the larger center compartment by a 1-in. hole, *c*, which can be closed by a stopper. When filled with water it overflows into the center compartment. These smaller compartments are intended to be used for collecting gases. When in use it is not necessary to stop up the whole sink and make it entirely useless to all other students.

The sink is designed to be used by four students, two on either side of the desk. Three water faucets, *a*, *a*, *b*, are illustrated. *a* and *a* are small and tapering, making them especially adapted for attaching rubber tubing for condensers, etc.

The sink is made of albarine stone and as illustrated is 32 in. \times 16 in. outside dimensions. The smaller compartments are 14 in. \times 5 in. \times 4 in. deep on the lower overflow side, which is 0.5 in. lower than the top of the sink. The larger compartment is 18 in. \times 14 in. \times 10 in. deep. The drain is in the middle of



the large compartment and is protected by a sieve. The size of the sink can be altered to suit any space.

Solvents for Phosgene¹

By Charles Baskerville and P. W. Cohen

COLLEGE OF THE CITY OF NEW YORK, NEW YORK, N. Y.

After the signing of the armistice, restrictions were placed on railroad transportation of liquefied phosgene in the United States. Previous to 1914 small cylinders of the liquid were imported from Germany to be used in producing a limited number of carbon compounds and for research purposes. It was produced in the country on a small scale after the blockade and before we entered the war, and was distributed in cylinders. Immense quantities were on hand when hostilities ceased. The greatest danger in the transportation of phosgene, liquid or in solution, would arise in case of fire or wrecks. Protection against leaky valves is quite simple.

While the demand for phosgene for the purposes mentioned is not great from the quantity point of view, nevertheless it exists. Oft expressed have been the hopes of finding more extensive uses for the poison gases of the World War in peace times. It seemed, therefore, worth while to endeavor to find other means for the transportation of and other applications for phosgene.

Among other qualifications, a liquid solvent for phosgene should be (1) inert to carbonyl chloride, (2) have a low vapor pressure, (3) hold notable amounts in solution, (4) admit of easy recovery of the gas, (5) preferably be nonflammable, and (6) involve minimum expense. The first and last of these qualifications are the most important, the former being primarily due to the reactivity of phosgene.

As a general statement it may be said that phosgene is soluble in ether, chloroform, liquid hydrocarbons,

carbon disulfide, and sulfur chloride, as well as in some of the liquid metal chlorides (stannic chloride and antimonie chloride).

The following liquids were used by us as solvents: carbon tetrachloride, chloroform, gasoline, paraffin oil, Russian mineral oil, benzene, toluene, glacial acetic acid, ethyl acetate, and chlorococane. The last substance is paraffin which has been melted and treated with chlorine. It forms a light yellow compound, the formula of which has not yet been determined. This compound is used medicinally to dissolve dichloramine-T.

The method of procedure was to pass the gas through a Bowen's absorption bulb containing the solvent at atmospheric pressure. The solution was stoppered well in a dry test tube and allowed to stand for 2 wks. Various tests were made on each solution to detect any evidence of reaction.

The following is a table of results for the solvents mentioned above:

SOLVENT	Weight Solvent Grams	Weight Phosgene Absorbed Grams	Solubility Ratio by Weight COCl ₂ :Solvent	Evidence of Reaction on Solution	Comments by Numbers Below
Carbon tetrachloride	79.5	22	1 : 3.6	None	1
Chloroform	49.4	29	1 : 1.7		2
Gasoline	37.0	30	1 : 1.2		3
Paraffin oil	34.6	0	0		4
Russian mineral oil	30.1	10.8	1 : 2.8		5
Benzene	43.9	43.6	1 : 1	None	6
Toluene	50.3	33.5	1 : 1.5		7
Glacial acetic acid	31.4	19.5	1 : 1.6		8
Ethyl acetate	20.5	20.2	1 : 1	None	9
Chlorococane	25.2	7.8	1 : 3.2	None	10

All weighings were made at 20° to 21° C. The ratio values are not given with mathematical accuracy for obvious reasons.

(1) With carbon tetrachloride no evidence of reaction was observed. The boiling point of the solvent was the same before and after saturation with phosgene.

¹ Presented before the Division of Industrial and Engineering Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

(2) and (3) In gasoline and chloroform, reactions were evidenced by heat of solution and change in boiling point.

(4) Paraffin oil was completely inert. No phosgene dissolved in it.

(5) Although Russian mineral oil did not show any evidence of reaction, it could not be used profitably because of the low solubility of phosgene in it.

(6) Benzene maintained the same boiling point before and after saturation. Phosgene and benzene in the presence of anhydrous aluminium chloride react to form benzoyl chloride and finally benzophenone. It was therefore undertaken to prove the absence of these substances in the solution of phosgene in benzene. Air was passed through a drying tower containing soda lime, and then through a solution of phosgene in benzene, through several U-tubes immersed in a freezing mixture, and finally through a solution of sodium hydroxide. The clean dry air, free of carbon dioxide, removed the phosgene from the benzene, the phosgene was liquefied in the U-tubes, and the excess air passed through the sodium hydroxide. At the same time if any hydrochloric acid were present in the benzene due to reaction, it would be carried over to the sodium hydroxide and there neutralized. The benzene free from phosgene was tested for benzoyl chloride and benzophenone by hydrolyzing with sodium hydroxide. A negative result was obtained. However, the sodium hydroxide in the train of apparatus was completely acidified, evidently due to phosgene which had been carried over. The benzene used in these experiments was not

free from thiophene. In saturating benzene with phosgene the solution increased in volume noticeably.

(7) Toluene showed a change in boiling point.

(8) Phosgene reacted with glacial acetic acid. Reaction was evidenced by heat of solution and an effervescence, also change of boiling point. This may have been due to a small amount of water in the acid.

(9) Ethyl acetate proved to be a solvent which closely rivaled benzene. It formed a 49.6 per cent solution with phosgene and was inert towards the latter.

(10) Chlorococane was inert and a fairly good solvent. However, it was not quite so good as benzene and ethyl acetate.

The vapor pressure of the saturated solution exerted at 20° C. was one atmosphere, while at 50° C., or the temperature of a hot sun, a further pressure of 308 mm. mercury or about 6 lbs. to the sq. in. developed. The problem of containers, therefore, is not serious. On heating the solution the phosgene is readily, and may be completely, driven off. Of the solvents tried, the two which gave most promise are benzene and ethyl acetate. Of these, benzene is probably the better, because it has a lower vapor pressure and is cheaper.

The imagination allows of possibilities of practical uses for such solutions in ridding lawns, etc., of moles, and in "mopping up" rats and other vermin.

ADDRESSES AND CONTRIBUTED ARTICLES

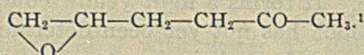
Studies on the Chemistry of Cellulose. I—The Constitution of Cellulose

By Harold Hibbert

DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT

(Concluded)

It is also of interest that 1-chloro-2-hydroxy butyl methyl ketone ($\text{CH}_2\text{Cl}-\text{CHOH}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{CH}_3$) when boiled with alkali does not yield the oxide

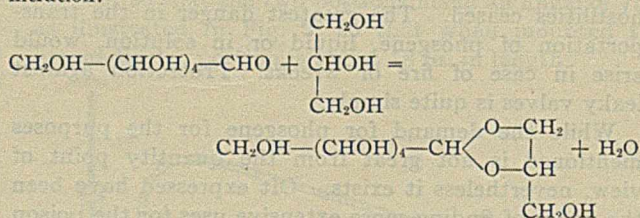


With respect to the second point, namely, the nitration of glycerol-sugar mixtures, it is known that the nitrogen content of these nitrated products is considerably lower than that of pure nitroglycerin. From the values customarily obtained in technical practice it would seem that the results are in general agreement with the assumption of a primary dehydration of the sugar molecule with the loss of one molecule of water, whereby two of the hydroxyl groups disappear, the remaining three undergoing nitration.

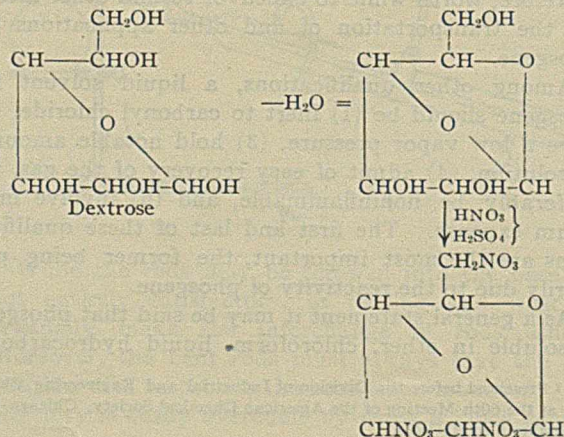
Recently it has been found possible, as indicated in the second part of the paper, to carry out some work on this subject.² It was found that when pure dextrose or cane sugar is dissolved in glycerol and nitrated with the usual $\text{H}_2\text{SO}_4\text{-HNO}_3$ glycerol nitrating mixture, the resulting nitrated product, judged from the nitrogen content, appears to contain only six nitrate groups, although there were eight hydroxyls originally present, *viz.*, five in the dextrose and three in the glycerol molecule. The same is true if we substitute a glycol for glycerol. In this case the

nitrogen content corresponds to only five nitrate groups, although the original mixture contained a total of 7 hydroxyl groups. How can such results best be explained? There are two possibilities:

1—The dextrose may undergo an *intermolecular* condensation with the glycol or glycerol, leaving six OH groups susceptible to nitration:



2—The dextrose may undergo, under the influence of the acid, an *intramolecular* condensation, to give a product, isomeric with



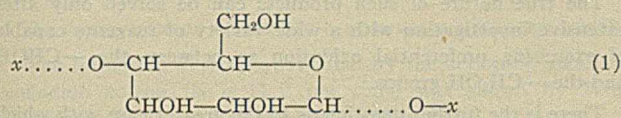
¹ Henry, *Bull. acad. roy. belg.*, [3] 36 (1898), 31; *Chem. Zentr.*, 1898 (2), 663. No indication is given as to the nature of the bodies formed and the subject is being investigated under the writer's direction by Mr. J. A. Timm.

² This work was carried out by Mr. R. R. Read at the Bureau of Mines, Pittsburgh, and the writer wishes to express his kindness to him for the assistance rendered; also to express his gratitude to Major Fieldner, Supervising Chemist, for kind permission to use the laboratory facilities.

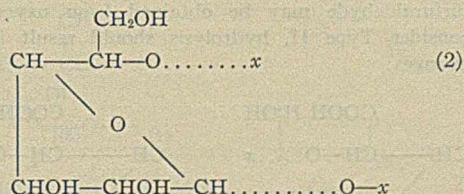
the cellulose nucleus, which then undergoes nitration to form a trinitrate. In view of what has already been said with respect to the constitution of hydroxy-aldehydes and ketones and the ease of formation of the γ - and δ -oxide types it seems possible that the changes represented (p. 334) might occur, thus opening up the possibility of the presence of a body isomeric, if not identical with, the trinitrate of the cellulose nucleus.

Which of the two views is correct can be decided only by further experimentation, and it would seem that determinations of the lowering of the freezing point of pure nitroglycerin by such products should enable a decision to be reached.

The transformation of the simple molecule into the highly polymerized product may take place by means of the opening of either a 5- or a 6-membered ring to give

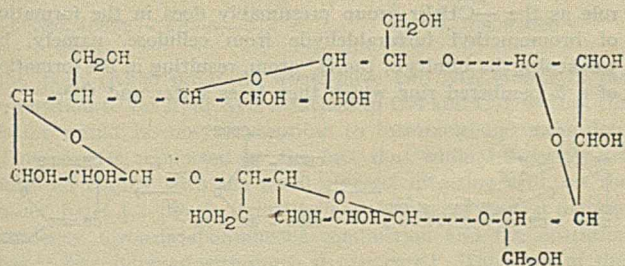


or



in which $x-x$ represent additional cellulose molecules.

As is indicated later, the balance of evidence is in favor of Formula 2, according to which cellulose is to be regarded as a dextrose glucoside of dextrose. It may be represented more fully as:



Such a theory can, of necessity, be of value only if in agreement with the experimental facts, and any proposed formula for cellulose must be capable of explaining not only the reactions quoted by Green,¹ but also the following:

11—Relation of cellulose to the cellulose nucleus.

12—The formation of 1,2,5-trimethyl glucose and the absence of a tetramethyl derivative by the action of dimethyl sulfate and subsequent hydrolysis of the methylated product (Denham and Woodhouse).

13—The formation of dextrose and cellobiose by the hydrolysis of cellulose acetate.

14—The production of levoglucosan by the action of heat on cellulose, starch, and β -glucose under diminished pressure.

15—Formation of ω -hydroxymethyl furfuraldehyde on distillation.

16—Action of metallic salts such as zinc chloride.

17—Formation and properties of hydrocellulose and cellulose hydrates.

18—Action of acids.

19—Relation of cellulose to starch and dextrose and the problem of plant metabolism.

These will now be discussed in the light of the proposed new formula.

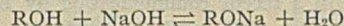
1,2—CELLULOSE NITRATE AND ACETATE

The formula indicates that the highest nitration product should

be a trinitrate and the highest acetyl derivative the triacetate, both of which facts are in agreement with the experimental evidence, higher values than the triacetate being associated with a partial disintegration of the cellulose molecule.

3,4—ACTION OF ALKALIES AND XANTHATE FORMATION

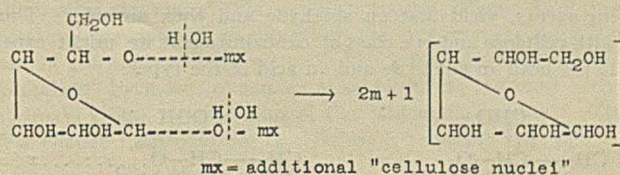
It is unnecessary to assume, as Green does, that the action of alkali on cellulose results in the opening of one of the rings, the behavior corresponding more nearly to that of a mixture of any alcohol with sodium hydroxide in which we have an equilibrium of the type:



This should be capable of reacting with carbon disulfide in a manner similar to that of any alkali, and in view of the pronounced tendency of alcoholic solutions of potash to undergo atmospheric oxidation, the increased tendency in this respect of an alkaline solution of cellulose xanthate is only what might be expected.

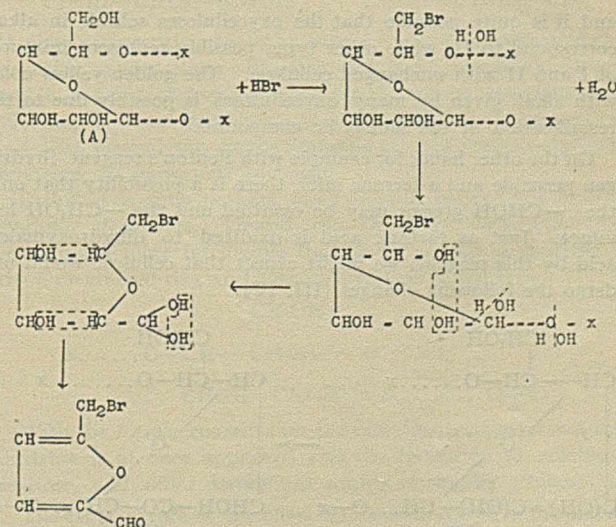
5,6—ABSENCE OF CARBONYL GROUPS, AND HYDROLYSIS WITH ACIDS

As already stated, the quantitative conversion of cellulose to dextrose is now a well-established fact and is of fundamental importance as a guide to the nature of the cellulose molecule. The change may be represented:



7—FORMATION OF ω -BROMOMETHYL FURFURALDEHYDE

Using the new configuration (A), in which the cellulose nucleus is assumed to have polymerized by the opening of the 6-membered ring, the changes taking place may be assumed to occur as follows:



in which the reactions are indicated by reference to the transformation of the polymerized product.

The first change is assumed to be the formation, from the primary alcohol grouping, of a bromide and water, followed by the addition of water and its subsequent removal, in the 1,5-position, the latter being facilitated by the influence of the bromine. A 5-membered ring thus results, which then undergoes depolymerization and dehydration as indicated.

¹ See Part I, THIS JOURNAL, 13 (1921), 257.

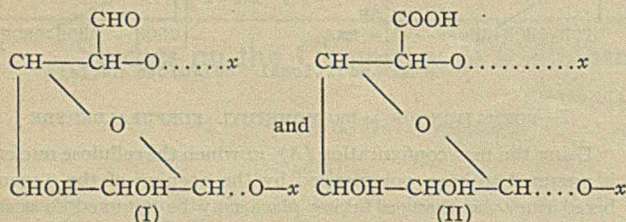
A reaction of this type in which the yield does not amount to more than 26 per cent of the theory cannot be regarded as of the same fundamental importance as one in which the yield is quantitative, as in the case of dextrose formation.¹

8—FORMATION AND PROPERTIES OF OXYCELLULOSE

The information contained in the literature regarding the properties of oxycellulose is both conflicting and confusing. Depending upon the type of oxidizing agent used and the conditions employed, a widely different type of product is obtained, the solubility of which in alkali, for example, varies within very wide limits. In a recent communication by Bancroft² on the oxidizing action of nitric acid, hypochlorites, permanganates, and chloric acid on purified cellulose, the conclusion is reached that there is only *one* oxycellulose, all the different products described in the literature probably representing mixtures of unchanged cellulose with oxycellulose. This view is based on similarity of properties, and especially on the fact that further treatment with the oxidizing agent of the product left after extraction with alkali gives an increased yield of alkali-soluble product.

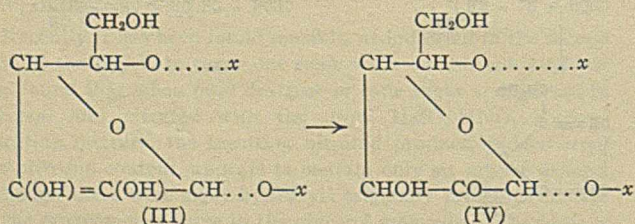
Considered from the new structural point of view, it is evident that with three hydroxyl groups there is a considerable number of possibilities.

In the first place it would seem that the $-\text{CH}_2\text{OH}$ group, being a primary alcoholic group, may, on treatment with oxidizing agents, yield first an aldehyde and then an acid. Thus, with cellulose and one class of oxidizing agent we might expect to get both an aldehyde and an acid of the types:



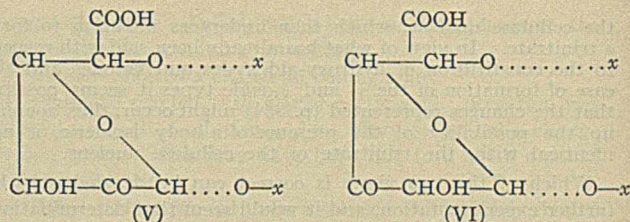
and it is quite possible that the oxycelluloses soluble in alkali correspond to II, while other types possibly represent mixtures of I and II with unchanged cellulose. The golden yellow color with alkali given by many oxycelluloses is possibly due to the resinification of the aldehydic compound.

On the other hand, for example with Fenton's reagent (hydrogen peroxide and a ferrous salt), there is a possibility that only the $-\text{CHOH}$ groups may be oxidized and the $-\text{CH}_2\text{OH}$ left intact. Just as tartaric acid is oxidized to dihydroxymaleic acid by this reagent, we might expect that cellulose would undergo the following changes (III, IV):



which would give an oxycellulose insoluble in alkali.

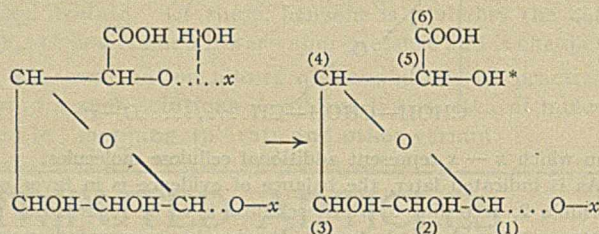
Finally, both types of oxidation may, and possibly do, take place at the same time to give oxycelluloses of the types V and VI:



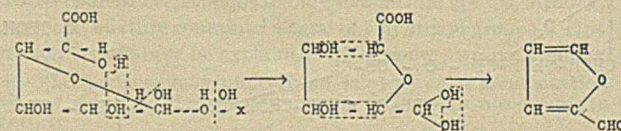
From the above standpoint, the view of Bancroft (p. 166) that "it is thus clear that the so-called insoluble oxycellulose is really unoxidized cellulose" cannot be considered as conclusively established.

The true nature of such products can be solved only after extensive investigation with a wide variety of reagents capable of exercising preferential oxidation as between the $-\text{CHOH}$ and the $-\text{CH}_2\text{OH}$ groups.¹

There is the further question as to the greater ease with which furfuraldehyde may be obtained from oxycellulose. If we consider Type II, hydrolysis should result in the following changes:

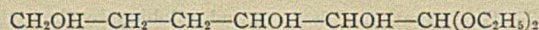


The carboxyl group attached to C-5 may then play the same role as the $-\text{CH}_2\text{Br}$ group presumably does in the formation of bromomethyl furfuraldehyde from cellulose, namely, by weakening the affinity of the H^+ atom, resulting in the formation of a 5-membered ring which then loses water and CO_2 :



It is, on the other hand, much more difficult to postulate any such series of reactions with an oxycellulose in which the oxidation of either of the $-\text{CHOH}$ groups is involved. Assuming that the latter could be oxidized, leaving the $-\text{CH}_2\text{OH}$ group intact, we might expect to get a type of oxycellulose insoluble in alkali and yielding practically no furfuraldehyde on treatment with acids.

Presumably an investigation of the behavior of a substance of the type



(in which the number and position of the hydroxyl groups correspond to those in cellulose) toward a variety of oxidizing agents would throw much light on the nature of the oxycelluloses.

9—FORMATION OF DIOXYBUTYRIC AND ISOSACCHARIC ACIDS FROM OXYCELLULOSE

Tollens and Faber,² by the action of calcium hydrate on an oxycellulose prepared by the use of dilute nitric acid according to the method of Cross and Bevan,³ were able to isolate from the mixture calcium dioxybutyrate and isosaccharate. The former they assumed to be derived from either

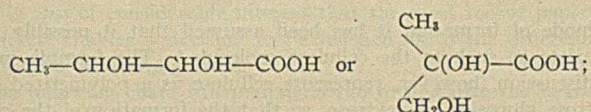
¹ Cross and Bevan ("Cellulose," 1918, Appendix, 334) are apparently still unreconciled to such a point of view.

² J. Phys. Chem., 19 (1915), 159.

³ The investigation of this interesting subject is being continued at Cornell University under the guidance of Professor Bancroft.

⁴ Ber., 32 (1899), 2594; von Faber, Dissertation, Göttingen, 1899.

⁵ J. Chem. Soc., 43 (1883), 22; 46 (1884), 206, 291, 897.

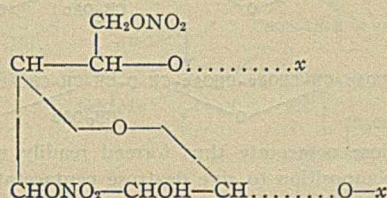


the latter, from $\text{CH}_2\text{OH---CHOH---CH}_2\text{---C(OH)} \begin{array}{l} \text{CH}_2\text{OH} \\ \text{COOH} \end{array}$

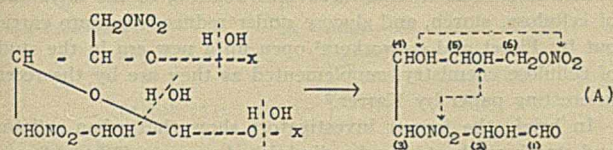
In the present state of our knowledge it is not possible to trace the course of such reactions, but with the accumulation of further experimental data regarding the chemical constitution of the oxycelluloses, and assisted by the wonderful researches and speculations of Nef¹ on the saccharic acids, much light should be shed on the nature of these changes.

10—FORMATION OF OXYPYRUVIC ACID FROM NITROCELLULOSE

The formation of oxypyruvic acid by the action of alkali on collodion cotton (N = 11.2 per cent) was shown by Will.² Assuming the latter to have the constitution

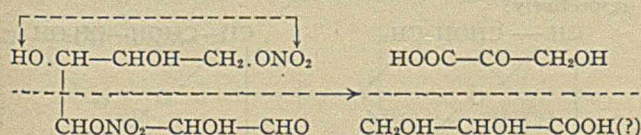


and to undergo hydrolysis according to the following scheme:



the body (A) so produced would have two NO_2 groups in the γ -position to the hydroxyls attached to C-4 and C-5, so that the latter would be very susceptible to intramolecular oxidation. This view is supported by the fact that while 1,2-glycols are nitrated readily with the usual glycerol nitrating acid, on the other hand 1,3-glycols (trimethylene, butylene) show a marked tendency towards spontaneous combustion and the operation has to be conducted with much greater care.³ The cause of this is in all probability the primary formation of mononitrate, in which the NO_2 group, being in the γ -position to the hydroxyl, exercises spatially a marked influence in increasing the tendency towards oxidation of the latter.

With the cellulose dinitrate, if we assume a similar influence of the NO_2 groups, oxidation of the γ hydroxyls should occur, which, together with a splitting of the ring and saponification, should yield oxypyruvic acid:



It is not necessary to assume that hydrolysis of the cellulose nitrate occurs prior to the oxidation process; presumably all of these changes occur together.

The difference in the behavior towards alkalis of cellulose nitrates on the one hand, and of the acetates on the other, would seem to be in harmony with this point of view. In the case of the acetates there is no tendency towards intramolecular oxidation and, as is well known, the cellulose is regenerated in the form of hydrate.

¹ Ann., **357** (1907), 214; **376** (1910), 1.

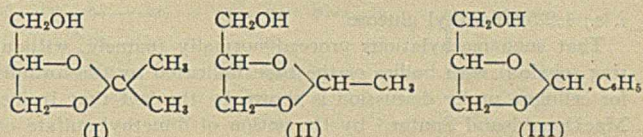
² Ber., **24** (1891), 400.

³ Author's unpublished researches.

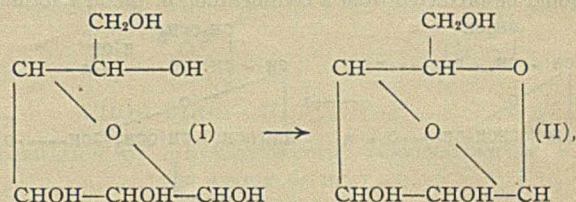
11—RELATION OF CELLULOSE TO THE CELLULOSE NUCLEUS

The nature of the linking by means of which polymerization takes place is of the greatest importance, since the properties of cellulose are in large measure controlled by it.

It is well known that the tendency toward formation of 5-membered rings containing oxygen is greater than that of 6-membered, and that with similarly constituted bodies the latter are less stable than the former. This is shown clearly in the condensation of polyhydroxy derivatives with carbonyl compounds. Thus, when acetone, acetaldehyde, benzaldehyde, etc., condense with glycerol, 5- and not 6-membered rings are formed:¹

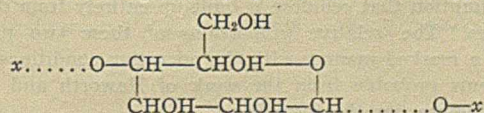


The tendency towards polymerization is invariably related to the outstanding residual affinity of one or more atoms in the molecule, and with dextrose the principal seat of this is to be found in the "aldehyde residue." The hydroxyl group associated with this in the dextrose molecule is in a more reactive condition than either of the other four, as seen in glucoside formation, and it may be assumed that the plant will, therefore, utilize this as the starting point for the next step in the synthesis of cellulose. A consideration of the phenomena of plant life emphasizes the remarkable tendency towards glucosidic formation, and the simplest way in which this can be exercised in the case of glucose would appear to be by "intramolecular glucosidic formation" by means of condensation involving the most active hydroxyl group, namely, that of the "aldehydic residue." The first change from dextrose to cellulose is probably that of



II thus representing to some extent a type of intramolecular glucosidic condensation. Whether this body is actually formed and is capable of free existence could best be ascertained by effecting its direct synthesis. It is possible that it may not be, but that instead the simple molecule at once undergoes polymerization, as indicated previously.

Cellulose is thus nothing more than a polymerized dextrose glucoside of dextrose. Viewed from this point its reactions become much more intelligible than if we assume a splitting of the 5-membered ring and a polymerization of the type:



With the former constitution the quantitative conversion into dextrose is at once apparent, and the formation of cellobiose, maltose, and other derivatives admits of simpler explanation.

The exact nature of the chemical forces involved in the polymerization process is a matter of speculation. According to Staudinger² the same forces operate in polymerized products as in the ordinary valence type of compound while, on the other

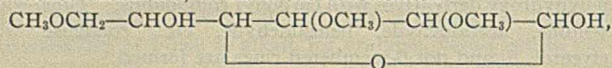
¹ Irvine, Macdonald and Soutar, *J. Chem. Soc.*, **107** (1915), 337; Irvine and Patterson, *Ibid.*, **105** (1914), 898; Peacock, *Ibid.*, **107** (1915), 815; Fischer, *Ber.*, **27** (1894), 1536; **28** (1895), 1167, 2496. In a recent paper (posthumous) by E. Fischer and E. Pfäehler [*Ber.*, **53** (1920), 1606] it is shown that acetone does not condense with trimethyleneglycol under similar conditions.

² *Ber.*, **53** (1920), 1073.

hand, Hess¹ is inclined to emphasize the part played by "partial valencies" as applied in the sense of Werner's theories.

12—NUMBER OF HYDROXYL GROUPS IN CELLULOSE AND THEIR RELATIVE POSITION (FORMATION OF 1,2,5-TRIMETHYL GLUCOSE)

The trimethyl glucose obtained by Denham and Woodhouse by the action of dimethyl sulfate on cellulose appears, from the evidence submitted, to have the constitution

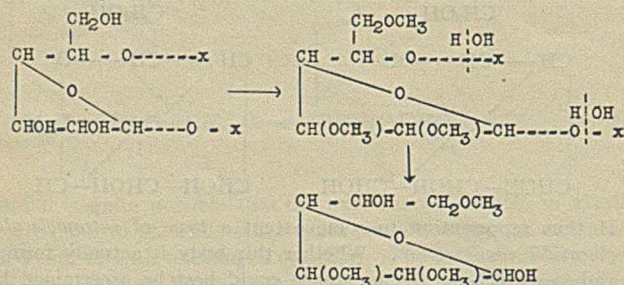


i. e., 1,2,5-trimethyl glucose.

That such methylations proceed normally (namely, without ring scission) with bodies of the type indicated by the formula for cellulose under discussion is shown by the fact that Irvine, MacDonald and Soutar,² by the action of dimethyl sulfate on isopropylidene glycerol in alkaline solution, were able to obtain a good yield of the α -methoxy derivative, in spite of the fact that the isopropylidene glycerol derivative is a relatively unstable substance.

It is somewhat improbable with such a powerful methylating agent as dimethyl sulfate that one of the hydroxyl groups in the cellulose molecule would remain unacted upon, and the fact that no indication (or only the merest trace) of a tetramethylglucose was obtained by these authors serves to establish the position and character as well as the number of the hydroxyl groups, and is a fact of fundamental importance in arriving at a decision as to the constitution of cellulose.

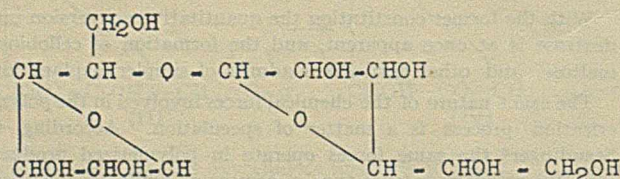
None of the formulas previously considered indicates the presence of a primary alcohol group. On the other hand, the formation of the trimethyl glucose in question is exactly what would be predicted from a consideration of the new formula:



13—FORMATION OF CELLOBIOSE AND DEXTROSE

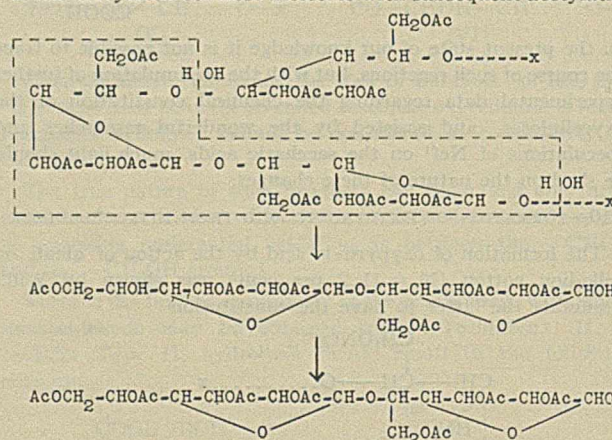
When cellulose is treated with a mixture of acetic anhydride, glacial acetic acid, and a small amount of sulfuric acid, it is converted into a mixture of cellobiose octacetate and dextrose pentacetate. Ost,³ as already stated, was able to obtain a combined yield of both, equivalent to 90 per cent, calculated on the assumption that cellulose is built up entirely from dextrose molecules. The relative proportions of these two products vary in a marked manner with the operating conditions.

It seems probable from the work of Haworth and Leitch⁴ that cellobiose has the formula



i. e., it is a dextrose glucoside of dextrose, and in view of its

mode of formation it has been assumed that it possibly pre-exists as such in the cellulose molecule.¹ The formula under discussion, however, represents cellulose as a polymerized dextrose glucoside of dextrose, so that the formation of the cellobiose octacetate may be represented as a simple disintegration of the acetylated cellulose molecule with subsequent acetylation:



The cellobiose octacetate thus formed readily undergoes secondary decomposition to give dextrose pentacetate.

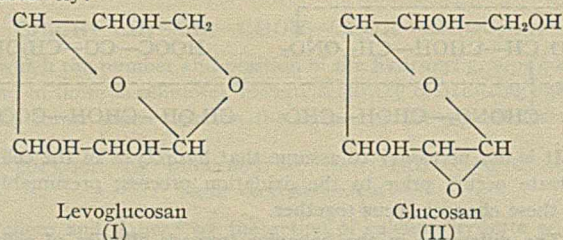
14—ACTION OF HEAT ON CELLULOSE

The recent remarkable discoveries relating to the distillation of cellulose, starch, and glucose under reduced pressure carried out by Pictet and co-workers² open up a new era in the study of cellulose chemistry, supplemented as they are by the recent interesting paper by Karrer.³

In brief, the former investigators show that when cellulose and starch are heated under diminished pressure (12 to 14 mm.) to a temperature of about 210° a yield of about 40 per cent of levoglucosan ($\text{C}_6\text{H}_{10}\text{O}_5$) is obtained. It was not found possible to obtain the same product by subjecting ordinary (α) glucose to the same treatment. When, however, β -glucose was so treated, Karrer was able to show that a similar high yield of levoglucosan is obtained.

On the other hand, Pictet and Castan³ found (in agreement with the work of Gélis)⁴ that α -glucose yields glucosan ($\text{C}_6\text{H}_{10}\text{O}_5$) on similar treatment. Both glucosan and levoglucosan have the same empirical formula ($\text{C}_6\text{H}_{10}\text{O}_5$), they are monomolecular, soluble in water, and contain three hydroxyl groups but no free carbonyl group. When levoglucosan is heated at a somewhat lower temperature (180°) in presence of platinum black, it is converted into dextrin.

A further investigation of the properties of these two interesting products⁵ shows that they possess Formulas I and II, respectively:



¹ If such were the case it would naturally have a very important bearing on the constitution of cellulose for, as pointed out recently by Hess, a constant ratio should be found to exist between the amounts of dextrose and cellobiose formed on hydrolysis. The important contribution of this author was received only after the present article had been communicated, and a short discussion of it is included as an appendix.

² *Loc. cit.*

³ *Helvetica Chim. Acta*, **3** (1920), 645.

⁴ *Compt. rend.*, **51** (1860), 331.

⁵ *Helvetica Chim. Acta*, **3** (1920), 640, 645.

¹ *Z. Elektrochem.*, **26** (1920), 232. In this connection see criticism by P. Karrer, *Helvetica Chim. Acta*, **3** (1920), 620, and reply of Hess, *Ibid.*, **3** (1920), 866; also discussion in appendix to this paper.

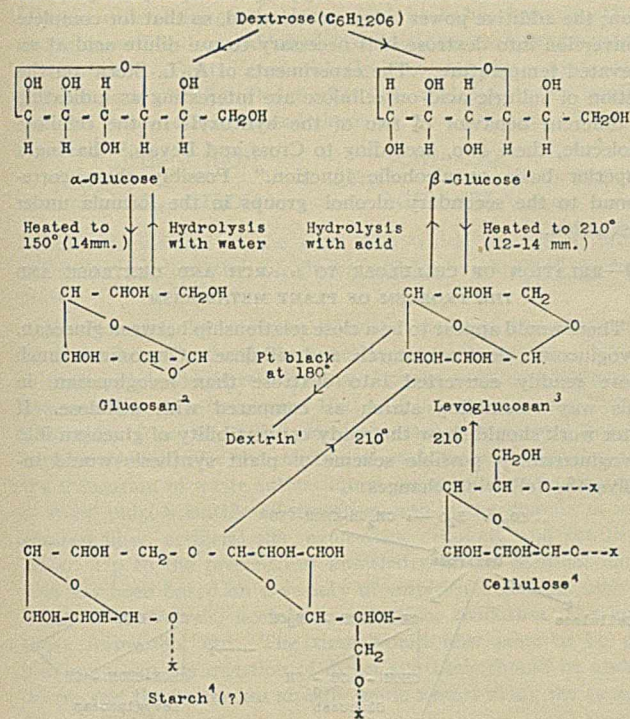
² *J. Chem. Soc.*, **107** (1915), 337.

³ *Loc. cit.*

⁴ *J. Chem. Soc.*, **113** (1918), 188; **115** (1919), 809.

It is also of considerable interest that the most recent paper of Pictet¹ enables a decision to be reached as to the different structure of α - and β -glucose.

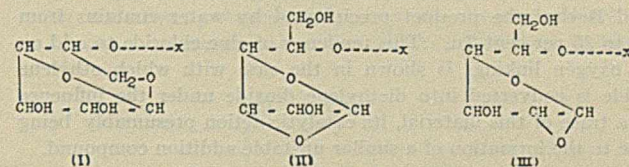
The following chart will perhaps serve to visualize the bearing of these important discoveries on the constitution of cellulose and their relation to the formula under discussion:



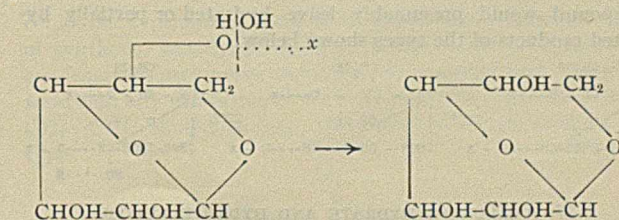
The emphasis placed throughout the present article on the fundamental importance of the carbonyl group thus seems to be warranted when it is borne in mind that three of the possible reactions into which the dextrose aldehyde group can enter are known to occur (see bottom of preceding column).

In considering the action of heat on cellulose the first point of attack will presumably be the most susceptible part of the molecule, namely, the "aldehyde residue."

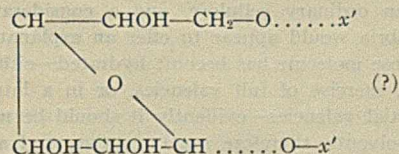
If scission takes place here, there are three possibilities for secondary ring formation:



Apparently at the higher temperature Formula I represents the most stable configuration, so that on further pyrolysis levoglucosan is obtained.



This, as shown by Pictet, on heating with platinum black¹ at a somewhat lower temperature, polymerizes into dextrin:



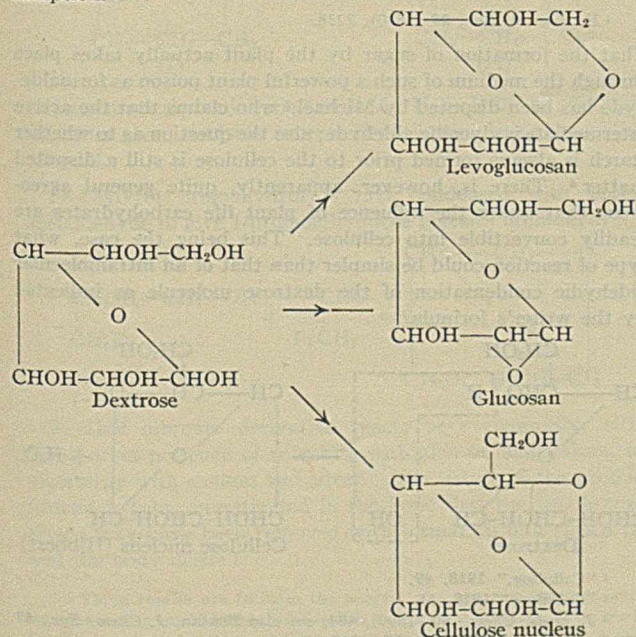
¹ Pictet, *Loc. cit.*

² Pictet and Castan, *Loc. cit.*

³ Pictet and Cramer, *Loc. cit.*

⁴ Pictet and Sarasin, *Loc. cit.*

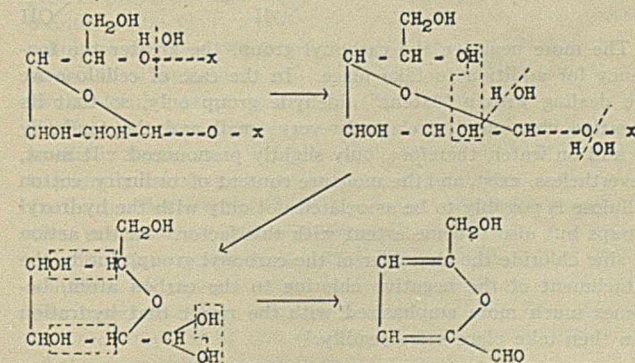
If we assume that starch possesses the constitution shown (and its quantitative conversion into maltose would indicate this to be the case), then starch must represent a polymerized form of levoglucosan, and the ease with which the latter is converted into dextrins, closely related to starch, bears out this assumption.



15—FORMATION OF ω -HYDROXYMETHYL FURFURALDEHYDE BY THE ACTION OF HEAT

It was shown by Erdmann and Schaefer¹ that when cellulose is subjected to dry distillation ω -hydroxymethyl furfuraldehyde is formed and may be isolated from the products of distillation.

Its formation probably takes place according to the scheme previously outlined for the production of ω -bromomethyl furfuraldehyde.

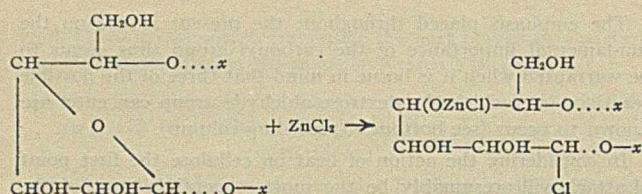


16—ACTION OF METALLIC SALTS (ZINC CHLORIDE, ETC.)

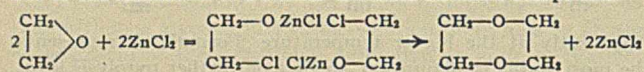
The solubility of cellulose in zinc chloride solutions is probably to be associated with the well-known tendency of the latter to form addition compounds with hydroxy and carbonyl derivatives:

¹ *Helvetica Chim. Acta*, **3** (1920), 649.

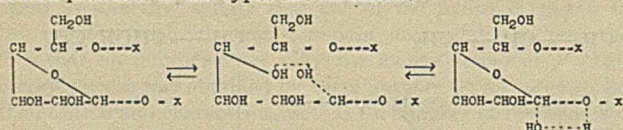
¹ *Ber.*, **43** (1910), 2391, 2398.



Such an unstable addition compound (assuming one molecule of zinc chloride attached to each dextrose residue) would contain 21 per cent Zn, calculated as such, and according to Cross and Bevan¹ the product precipitated by water contains from 18 to 25 per cent Zn. This tendency of zinc chloride to add on to oxygen linkings is shown in the ease with which ethylene oxide is converted into diethylene dioxide under the influence of a trace of this material, its catalytic action presumably being due to the formation of a similar unstable addition compound.

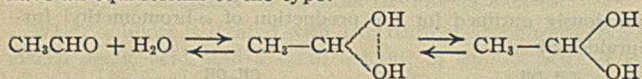


The addition of water to the zinc chloride-cellulose addition compound would presumably leave hydrated or partially hydrated products of the types shown below:



17—CELLULOSE HYDRATE AND HYDROCELLULOSE

It is well known that cellulose prepared from zinc chloride solutions represents a hydrated product which is much more reactive than ordinary cellulose, and a consideration of the above equilibria would appear to offer an explanation of this. If the cellulose molecule has become hydrated—either actually, through the exercise of full valencies, or in a latent manner through partial valencies—evidently it should be more soluble in various solvents, therefore more reactive, and at the same time should give acetyl and other derivatives of a higher order than three. That such an equilibrium mixture probably exists is supported by a consideration of the properties of aldehydes in general. Thus, with chloral the tendency to form a hydrate is so pronounced that the reverse change $\text{CCl}_3-\text{CH}(\text{OH})_2 \rightarrow \text{CCl}_3-\text{CHO} + \text{H}_2\text{O}$ scarcely comes into consideration. On the other hand, with acetaldehyde we probably have an equilibrium of the type:



The more negative the carbonyl group, the greater the tendency for addition to take place. In the case of cellulose we are dealing with a "latent" aldehyde group only, so that its negative character is relatively very small and the tendency to add on water, therefore, only slightly pronounced. It must, nevertheless, exist, and the moisture content of ordinary cotton cellulose is possibly to be associated not only with the hydroxyl groups but also to some extent with this factor. In the action of zinc chloride the character of the carbonyl group, due to the attachment of the negative chlorine to the carbon atom, becomes much more emphasized, with the result that hydration can then take place more readily.

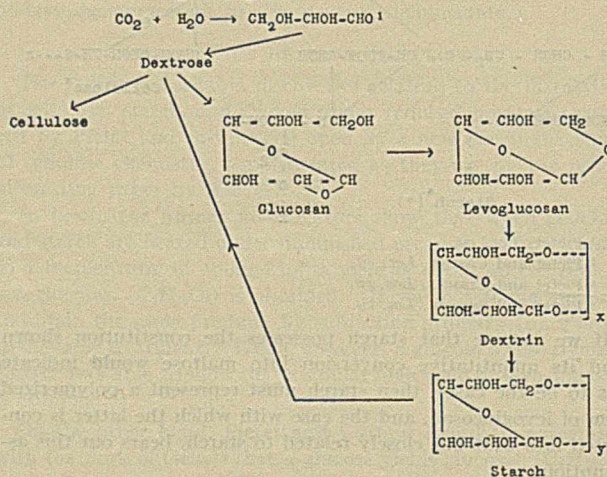
18—ACTION OF ACIDS

The remarkable ease with which cellulose is resolved quantitatively into dextrose under the influence of highly concentrated aqueous hydrochloric acid² is a strong argument for the close relationship existing between them. Its behavior falls into line with that of any other glucoside, and to this extent supports

that point of view as to its structure. The difference in behavior between concentrated sulfuric and hydrochloric acids is to be explained by their specific action. The latter is characterized by a greater ease of addition in general to oxygen linkings resulting in a depolymerization and ring opening. The former, on the other hand, is characterized by a greater power of dehydration; the additive power is less pronounced, so that for complete conversion into dextrose it is necessary to use dilute acid at an elevated temperature. The experiments of A. L. Stern¹ on the action of sulfuric acid on cellulose are interesting as indicating a different behavior of two of the hydroxyls in the cellulose molecule, these two, according to Cross and Bevan,² "having a superior basic or alcoholic function." Possibly these correspond to the secondary alcohol groups in the formula under discussion.

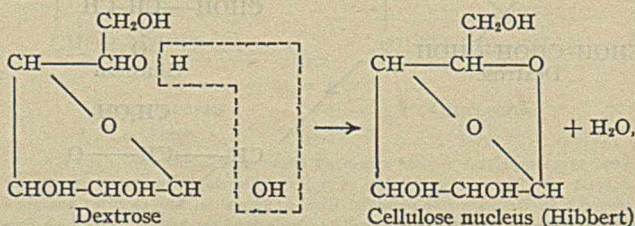
19—RELATION OF CELLULOSE TO STARCH AND DEXTROSE AND THE PROBLEM OF PLANT METABOLISM

There would appear to be a close relationship between glucosan, levoglucosan, dextrose, starch, and cellulose. Glucosan is much more readily converted into dextrose than levoglucosan, in this way resembling starch as compared with cellulose. If later work should show the ready convertibility of glucosan into levoglucosan, a possible scheme of plant synthesis would involve the following changes:



¹ E. Fischer, *Ber.*, 23 (1890), 2238.

That the formation of sugar by the plant actually takes place through the medium of such a powerful plant poison as formaldehyde has been disputed by Michael,³ who claims that the active intermediate is glycollic aldehyde; also the question as to whether starch is always formed prior to the cellulose is still a disputed matter.⁴ There is, however, apparently, quite general agreement that under the influence of plant life carbohydrates are readily convertible into cellulose. This being the case, what type of reaction could be simpler than that of an intramolecular aldehydic condensation of the dextrose molecule as indicated by the writer's formula?



¹ "Cellulose," 1918, 49.

² "Cellulose," 1918, 51.

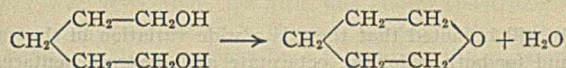
³ *J. prakt. Chem.*, 60 (1899), 484; see also Fenton, *J. Chem. Soc.*, 67 (1895), 780; 71 (1897), 375; 75 (1899), 575.

⁴ Cross and Bevan, "Cellulose," p. 73.

¹ "Cellulose," p. 8.

² Willstätter and Zechmeister, *Loc. cit.*

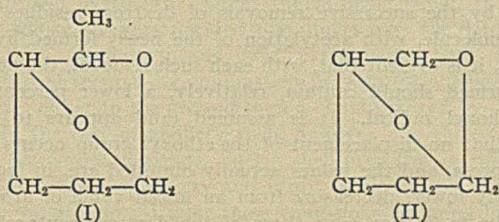
It is probably safe to say that the plant will work along lines involving the least expenditure of energy necessary to effect the required synthesis, and this would seem to correspond with the γ,δ -dihydroxy condensation shown above. The facility with which aldehydes and ketones condense *intermolecularly* with hydroxy derivatives to form 5- and 6-membered rings and the ease of *intramolecular* γ - and probably δ -condensation in the case of hydroxy-aldehydes and ketones both lend support to this view. Dextrose admittedly possesses the γ -oxide constitution and the knowledge that 1,4- and 1,5-glycols readily split off water to form closed rings:



is further evidence of the ease with which the above intramolecular condensation of glucose might be expected to take place.

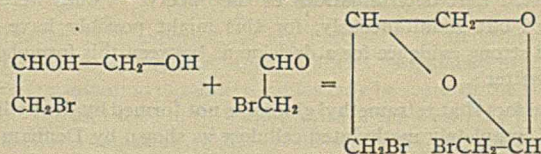
The necessity for a closer scientific study of the properties of the cellulose molecule becomes increasingly evident in view of the present pronounced shortage of paper pulp, and it does not seem unreasonable to assume that with a more extended knowledge of its chemical constitution important material will thereby become available for the solution of such technical problems as the utilization of waste sulfite liquor, improvements in the yield of wood pulp, scientific afforestation, and in the domain of vulcanized fiber, artificial silk, explosives, celluloid, and synthetic fuels. Up to the present our knowledge of the cellulose molecule has been based on a variety of empirical reactions such as those of hydrolysis, acetolysis, nitration, oxidation, the xanthate formation, etc. The time would now seem to be opportune when the question of direct synthesis should be undertaken, and the writer has already made a start along the general lines outlined below.

An examination of the new formula indicates the parent substance to be a body of Type I, while a still simpler derivative would be that indicated by II,



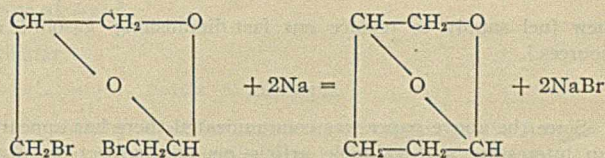
and attempts (in conjunction with Mr. H. S. Hill)¹ to synthesize the latter give promise of success, the following being the method adopted.

1—Glycerol bromohydrin is first condensed with bromoacetaldehyde to give 1-bromoethylidene glycerol bromohydrin,



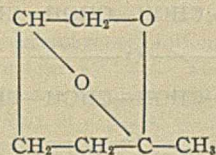
2—This dibromo derivative reacts very vigorously, either alone or in presence of solvents, with zinc or magnesium, less vigorously with sodium and silver. The nature of the products formed is being investigated in the hope that the two bromine atoms may have been removed with formation of a closed ring and the body desired.

¹ These results are to form the subject of a separate communication and the writer would like to reserve this field for the present. The work is being pushed as rapidly as the somewhat limited assistance at his disposal permits.

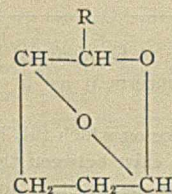


The product may be expected to yield on hydrolysis with dilute acids 3,4-dihydroxyvalerianic aldehyde, a fact which would be of considerable importance in its bearing on the constitution of cellulose.

By substituting bromoacetone for the bromoacetaldehyde in the above reactions, a body possibly closely related to inulin of the type



could be synthesized, and it is hoped this suggested mode of synthesis, namely, γ,δ -hydroxy aldehydo (respectively, keto) condensation may prove capable of wide application. It would seem that any derivative of the type $\text{R.CHOH—CHOH—CH}_2\text{—CH}_2\text{—CHO}$ should undergo condensation to the bridged ring type



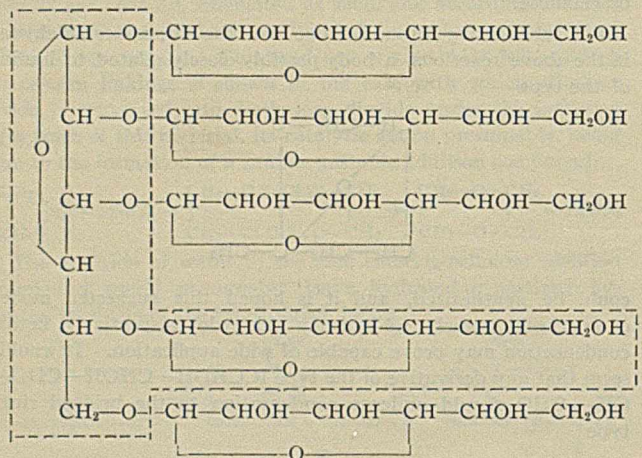
and the various aldehyde condensation products from crotonaldehyde, acrylic aldehyde, acetaldehyde, allyl acetone, etc., are being investigated from this standpoint. Coincident with such researches it would seem highly desirable, in view of our increased knowledge, to subject to careful reexamination many of the typical reactions of the cellulose molecule.

It cannot be too clearly indicated that the above speculations are all concerned with the nature of a product of plant metabolism, regarding which knowledge can be acquired only by patient, intensive research, involving a far-reaching study of its botanical, physical, and chemical nature. The degree of polymerization may, and probably does, vary with the nature of the plant metabolism and the reason why different celluloses do not show much greater variations in chemical behavior than they do, is that the energy relations of the atoms in two molecules, one of which is, say, $(\text{C}_6\text{H}_{10}\text{O}_5)_{75}$, and the other $(\text{C}_6\text{H}_{10}\text{O}_5)_{100}$, cannot be very different. The evidence at present available would seem to be against the idea of the entire cellulose family being representable by one large molecule $(\text{C}_6\text{H}_{10}\text{O}_5)_x$. In the purification treatment small amounts of various derivatives are removed, and such removals probably leave the molecule in a more active state, owing to the setting free of residual affinities, hitherto exercised in holding them in combination. The sensitiveness of cellulose to small changes may probably be accounted for in this manner. In conclusion, the subject of the constitution of cellulose and the scientific principles underlying its industrial applications calls for an intimate co-operation between plant physiologist, and organic and physical chemist. The former, by the elucidation of the nature of plant enzymes, may ultimately place the forester in the position of being able to improve materially the growth of trees, while from the union of the two latter forces many technical advances may be hoped for, not the least of which is that of obtaining a

new fuel supply to replace our fast-diminishing gasoline resources.¹

APPENDIX

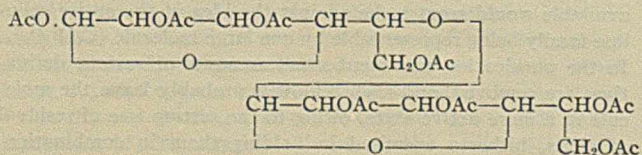
Since the above paper was communicated there has appeared an interesting and valuable article on this subject by Kurt Hess.² The author, from various considerations, one of which is the pronounced tendency of plants to form glucosides, arrives at the conclusion that the properties of cellulose are best explained by the formula:



Cellulose is accordingly to be regarded (at least in so far as the ground-structure is concerned) as a pentadextrose glucoside of dextrose.

The principal evidence on which this is based rests on the constant ratio assumed to exist between the amounts of cellobiose octacetate and dextrose pentacetate formed when cellulose is acetylated (under prescribed conditions) by acetic anhydride in presence of glacial acetic acid and a powerful catalyzer and dehydrating agent, *viz.*, concentrated sulfuric acid. By carefully regulating the conditions of acetylation, Ost³ was able to obtain a combined yield of 90 per cent of the theory calculated on the assumption that cellulose is made up entirely from dextrose molecules. The highest obtainable yield of cellobiose octacetate was 37.2 per cent of that theoretically obtainable (assuming cellulose to consist entirely of cellobiose molecules), this amount being found to vary considerably with the temperature, time of acetylation, amount of catalyst, etc. The values obtained do not support the view of a constant ratio between dextrose pentacetate and cellobiose octacetate formation.

If the conditions employed are such that no decomposition of the cellobiose acetate into dextrose acetate may be assumed to have taken place, and if acetylation occurs with scission of the molecule as outlined diagrammatically above, thus accounting for the formation of cellobiose octacetate, *viz.*,



then four molecules of glucose pentacetate would be formed to each one of cellobiose octacetate.

Hess gives the results obtained in eight experiments by several

investigators, and these are reproduced below. (On the above assumption, 9.38 g. of dry cellulose should give 6.42 g. of cellobiose octacetate and 12.51 g. dextrose pentacetate.)

Expt.	Wt. of Cellobiose Octacetate	Theory	Wt. of Dextrose Pentacetate	Theory
I ¹	5.3	6.42	6.4	12.51
II ¹	6.8	6.42	12.0	12.51
III ¹	7.3	6.42	12.4	12.51
IV ¹	7.08	6.42	10.4	12.51
V ¹	2.8	6.42	17.0	12.51
VI, VII, VIII ²	5.8; 5.9; 6.2	6.42	Not determined	12.51

¹ Ost, *Ann.*, **398** (1913), 323.

² Madsen, Dissertation, Hannover, 1917.

It will be noted that there is a wide variation in the values found for both cellobiose octacetate and dextrose pentacetate. Of fundamental importance (in view of the eminent standing of the author and his reiteration of the correctness of the work) are the high values for cellobiose octacetate obtained by Ost as indicated in Expts. II, III, and IV, and they seem to provide strong evidence against the soundness of Hess' views. Greater reliance is placed by the latter on Expts. VI, VII, and VIII, although it is unfortunate that no values for the glucose pentacetate are given. No explanation is vouchsafed for the remarkable course which the hydrolysis of the cellulose molecule is supposed to follow, and all that can be said at the moment is that the data submitted offer the possibility of a highly interesting relationship, which, if true, would necessarily have a marked bearing on the constitution of cellulose.

Of considerable importance are the results quoted by Hess and Wittelsbach in the same article on the acetylation of a sample of cellulose ethyl ether ($\text{OC}_2\text{H}_5 = 47.2$ per cent). This product was submitted to continued treatment at a low temperature with a mixture of acetic anhydride, and glacial acetic and strong sulfuric acids, and determinations made of the ethoxyl content of the products formed after given intervals of time. Under the conditions employed the cellulose ethyl ether was converted partly into acetylated dextrose-, partly into acetylated dextrin-ethyl ethers. On the theory that the latter are produced by the successive removals of dextrose residues in the Hess molecule, with acetylation of the newly formed hydroxyl groups, it is evident that, with each such removal, the new dextrin formed should contain, relatively, a lower percentage of the ethoxyl radical. It is assumed (and appears to be the case) that no displacement of the ethoxyl group occurs during the process, and the values actually obtained are, in fact, considerably lower, decreasing from an initial value of around 40 per cent to 26 per cent, those of the dextrose pentacetate remaining approximately constant. While these experiments furnish supporting evidence they cannot be accepted as supplying anything in the nature of final proof. In the first place, the values relate to dextrin derivatives, and our knowledge of these, as a class, is admittedly in a very hazy condition. It is to be regretted that determinations of the "acetyl" values were not carried out simultaneously, for this might possibly have provided strong evidence for a decision as between this formula and the writer's.

The fact that tetramethyl glucose is not formed by the hydrolysis of completely methylated cellulose as shown by Denham and Woodhouse is a strong argument against the Hess formula. These investigators were unable to identify any trimethoxy glucose other than the 1,2,5-derivative, although from a consideration of his (Hess') formula there seems to be no logical explanation as to why several isomeric trimethoxy derivatives should not be formed simultaneously. In view of the fact that the triethoxy cellulose used by Hess was apparently a mixture of di- and tri-derivatives, it seems advisable to have the work repeated with preparations made according to the Lilienfeld process and containing the equivalent of three (OC_2H_5) radicals calculated on the molecule $\text{C}_6\text{H}_{10}\text{O}_3$.

¹ The British government is already giving serious consideration to this subject and has appointed a special committee for this purpose. Of interest is the fact that last year the sum of \$90,000 was donated for research on cotton alone. The Cotton Association now proposes to raise a Research Fund of \$1,250,000.

² *Z. Elektrochem.*, **26** (1920), 232.

³ *Ann.*, **398** (1913), 323.

Combustion Smokes^{1,2}

By Geo. A. Richter

RESEARCH DEPARTMENT, BROWN COMPANY, BERLIN, N. H.

A new development of the late war with the Central Powers was the use of artificial smokes for obscuring purposes. The allied navies made early provision for smoke screens as part of their program for eluding the wily submarine, and in the later days used them in major offensive operations against the submarine bases. The armies also found it economical to lay down smoke barrages before taking the offensive. The first devices were very crude, for little was known concerning the physical properties of such clouds. Consequently, research was necessary along chemical lines to improve the smoke-producing substances themselves and also along mechanical lines to perfect the devices in which the smoke is generated. This paper concerns itself primarily with the chemical developments, which are known as combustion smokes.

In general, we may classify smokes according to the method of generation, as detonation smokes, cold reaction smokes, and combustion smokes. The first class is represented by a bursting shell containing oleum or sulfur trioxide, which creates a cloud by the disintegration of the substance into a screen or mist made up of a myriad of small particles. It takes its name from the detonating charge of TNT or similar explosive used to break it up. The well-known ammonium chloride smoke may be called a cold reaction smoke, because it results from interaction of two gases without appreciable heat change. The combustion smokes, on the other hand, involve exothermic reactions, which disseminate solid material into the air in the form of minute particles. This classification is of course artificial, and some smokes cannot be defined by it. For instance, the smoke produced by the detonation of phosphorus in a 3-in. shell represents both the detonation and the combustion types.

Combustion smokes are used to good advantage in grenades, candles, trench mortar shell, and in navy smoke boxes, designed to be thrown overboard. Other things being equal, the combustion smoke has very decided advantages over the detonation type. Both laboratory and field experiments have proved that a screen secured by combustion persists for a longer time and clings closer to the ground than a cloud realized by detonation. In the case of artillery shell, however, the choice is limited to the detonating type, since a shell fired from a rifled gun travels at enormous velocity and is apt to bury itself from 2 to 6 ft. in the ground. Under these conditions we must have an explosive charge of sufficient power to blow shell fragments and smoke producer from out the ground as desired. An attempt to utilize a combustion smoke in the artillery shell would result in a smothered combustion underground with no real screening effect.

LABORATORY METHODS

Although field experiments are necessary to determine the ultimate value of any substance or device as a smoke producer, a fair determination of relative values may be made in the laboratory. The unit used in the laboratories of the Chemical Warfare Service for comparing relative values of different smoke producers is called the "total obscuring power," or, in abbreviated form, the T.O.P. It is defined as the product of the volume of smoke produced from a unit weight of the original mixture and the density of the smoke. The density is the reciprocal of the depth of smoke layer beyond which it is impossible to distinguish clearly the filament of a 40-watt Mazda lamp. Since the English units are employed for most field work, they are retained for this purpose.

¹ Received February 15, 1921.

² Published by permission of the Chief of the Chemical Warfare Service.

The chamber used for actual measurements at the American University Experimental Station had a cubical content of 228 ft. In carrying out the determination, the mixture to be tested was placed on the floor of the box and ignited or disintegrated by a detonating charge. The smoke cloud was made of uniform density by means of an electric fan within the box. Readings with a movable pilot lamp were taken over a series of short intervals and the resulting data plotted. Such values as average of maximum T.O.P. could then be read from the curve obtained.

In the interpretation of results, T.O.P. measurements must be supplemented by a careful consideration of the type of device to be used and by actual service tests. The conditions affecting the persistency of a cloud in the open field are often very different from those prevailing in a closed chamber. For instance, it is still an open question whether phosphorus or sulfur trioxide is the more efficient substance to employ in artillery smoke shell, whereas laboratory measurements show the phosphorus to have twice the T.O.P. of sulfur trioxide. The sulfuric anhydride cloud, however, is cooler and has less tendency to rise.

PRELIMINARY WORK

The theoretical basis of American research on combustion smokes was the well-known fact that metals high in the electromotive series react with organic chlorides to form metallic chlorides, which are sublimed by the heat evolved. A mixture of carbon tetrachloride, zinc powder, zinc oxide, and kieselguhr showed greatest promise and was chosen as a point of departure. On ignition of this mixture, the exothermic reaction disseminates zinc chloride in the air in the form of cloud of fine solid particles, which have obscuring power. The zinc oxide and kieselguhr prevent segregation of components and stiffen the mass. They also serve to prolong the time of burning and to cool the smoke.

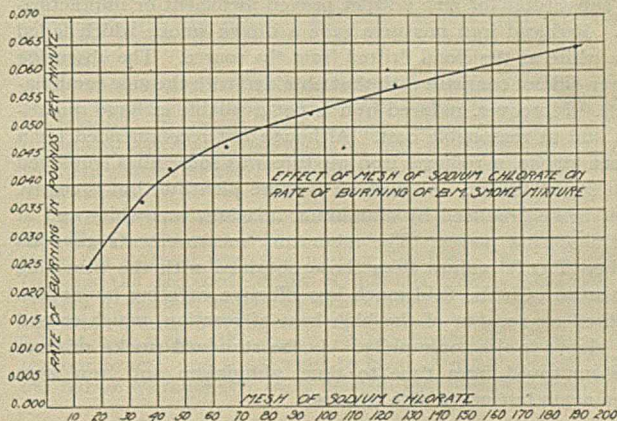


Fig. 1

The early mixtures of these four components, however, proved imperfect. The amounts of zinc oxide and kieselguhr that provided for fairly efficient burning only made a thin pasty mass. Although the light gray smoke produced had good obscuring power, the burning was very uneven and considerable residue was left.

THE IDEAL SMOKE MIXTURE

In order to follow a logical line of research, the following desirable features of a combustion smoke mixture were listed:

- 1—The materials must be cheap.
- 2—The materials must be obtainable in large quantities.
- 3—The mixture must be staple.

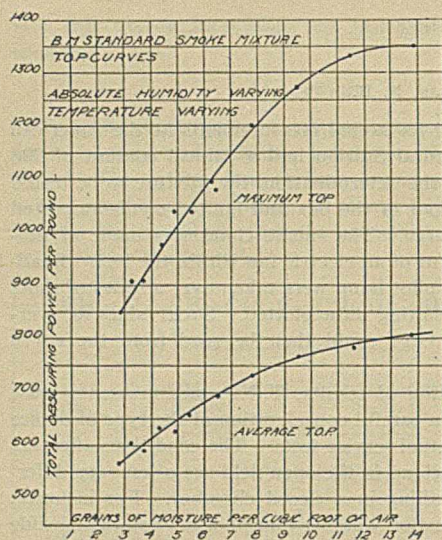


Fig. 2

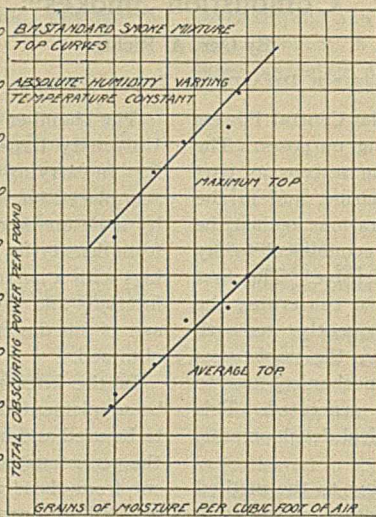


Fig. 3

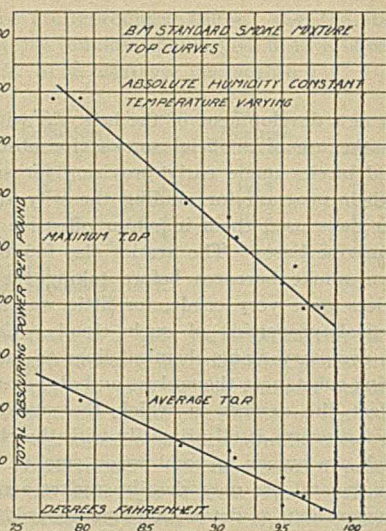


Fig. 4

4—The reaction rate must be subject to control, in order to obtain a predetermined fast or slow burning substance.

5—The smoke produced must have a high obscuring power.

6—The smoke produced must be comparatively cool, in order to slow down dissipation of the cloud.

The preliminary results suggested that five types of material were necessary.

1—A metal or metallic oxide capable of producing a readily volatile chloride.

2—An oxidizing agent.

3—A cooling material.

4—An absorbing substance.

5—A chlorinating agent.

CHOICE OF METAL

The metals seriously considered were zinc, iron, and aluminium. All substitutes for zinc powder proved inefficient or impracticable. Reduced iron mixtures gave a brown smoke which faded to a white as the cloud drifted from the source. The obscuring power did not compare with that obtained with the zinc combinations. Moreover, reduced iron is not available in large quantities and at reasonable cost. Although not recommended for a screen smoke, a reduced iron mixture was sometimes employed as a signal smoke. Aluminium is more plentiful, but is costly. The smoke produced by aluminium mixtures was white and of fair obscuring power. The laboratory measurements gave no higher T.O.P. values than those obtained with the best zinc mixtures. On the field much less effective covering power was realized on account of the high heat of reaction, which caused the clouds to rise too rapidly. As the standard smoke mixture was improved from time to time, aluminium and iron were tried again but never with success.

SELECTION OF OXIDIZING AGENT

Since white smokes have always proved more effective as screens, one of the criticisms of the first mixtures concerned their color. Although perchlorates and nitrates were tested to neutralize the carbon gray in the original components, sodium chlorate was finally selected for economic as well as chemical reasons. After a series of box and field experiments, a mixture of the following composition was selected:

	Parts
Carbon tetrachloride.....	35.0
Zinc powder.....	40.0
Zinc oxide.....	6.4
Sodium chlorate.....	9.0
Kieselguhr.....	9.6

Results with this mixture suggested the need of changing the cooling and absorbent ingredients. The smoke produced is white and has good obscuring power. In consequence of the high heat of reaction, however, the cloud formed is hot and rises rapidly. Therefore much of the theoretical T.O.P. is lost when burned in the open. Moreover, it is very difficult to control the time of burning due to arching over of the residues left.

CHANGE IN COOLING AGENTS

In order to cool the smoke, zinc oxide was replaced by ammonium chloride, which absorbs considerable heat by its volatilization and partial dissociation. The addition of ten parts of chloride caused a cooler cloud and increased the time of burning. The T.O.P. was correspondingly increased by the volatilized ammonium chloride. The modified mixture is represented by the following formula:

	Parts
Carbon tetrachloride.....	41.4
Zinc.....	35.4
Sodium chlorate.....	9.5
Ammonium chloride.....	10.0
Kieselguhr.....	3.7

One pound of this mixture packed in a can 3 in. in diameter burned in 2 min. The T.O.P. was from 1200 to 1700, while white phosphorus burned under the same conditions gave a value ranging from 4000 to 5000. Unsuccessful attempts were made to increase the amount of ammonium chloride.

REGULATION OF TIME OF BURNING

The substitution of ammonium chloride for zinc oxide did not eliminate the difficulty experienced in control of time of burning. An extensive investigation carried out with large quantities of the mixtures showed that the factors which most influenced the time of burning were mesh of chlorate crystals, percentage of ammonium chloride present, and the type of absorbent used. The finer the chlorate used, the more rapid was the burning. The curve (Fig. 1) showing the time of burning plotted against the mesh of the chlorate flattens somewhat with crystals above 40 mesh. Inasmuch as the change of rate between 40 and 60 mesh is less noticeable, this mesh was usually specified. Mixtures were often calibrated by changing the amount of chloride in the formula.

The use of kieselguhr as an absorbent proved to be the source of many irregularities. During burning it had a tendency to

arch over the combustion surface, causing successive periods of slow and fast burning. Moreover, surveillance tests in the laboratory showed a reaction between carbon tetrachloride and zinc. This deterioration was due to the moisture from the kieselguhr, and ammonium chloride acted as a further catalyzer.

A precipitated magnesium carbonate was fully as efficient as kieselguhr. Its substitution for kieselguhr provided for stability under conditions encountered in transport. Its gradual decomposition by heat made for smoother burning. Magnesium carbonate was employed in practically all the zinc chloride smoke mixtures recommended.

CHLORINATING AGENTS

The advantages of substituting a solid chlorinating agent for carbon tetrachloride were realized from the first. Silicon and titanium tetrachlorides were found to offer no added advantage over carbon tetrachloride. Mixtures containing the silicon compound were peculiarly sensitive, a single drop of water being sufficient to start the reaction.

B. M. SMOKE MIXTURE

The final mixture was called the B. M. smoke mixture, because it was perfected while the American University Experimental Station was still under the Bureau of Mines. The proportions in the following representative formula were varied somewhat, depending on the method and form of device in which the smoke was to be used:

	Parts
Zinc.....	35.4
Carbon tetrachloride.....	41.6
Sodium chlorate.....	9.3
Ammonium chloride.....	5.4
Magnesium carbonate.....	8.3

INFLUENCE OF WEATHER CONDITIONS

T.O.P. measurements in the chamber revealed the fact that weather conditions have a marked influence on the efficiency of the B. M. mixture. Increasing the moisture content of the air raises the T.O.P., while an increase of temperature reduces the T.O.P. When both moisture content and temperature are raised in proportions that may be ordinarily expected in the field, the result is an increased T.O.P. value. Figs. 2, 3, and 4 show the rate of change in T.O.P. under different conditions. In this work the T.O.P. values were taken at 7-min. intervals. The curves give the changes in both the maximum T.O.P. and the average T.O.P. obtained over this period. The average T.O.P. is easily calculated by integration between the fixed limits of the area under the curve.

It is thus evident that the most efficient smoke is produced from the B. M. mixture on a cold, damp day, whereas the poorest cloud results on a warm, dry day. These observations in the T.O.P. chamber were confirmed by field experiments. The increase of obscuring power with humidity is apparently due to absorption of water by the hygroscopic zinc chloride particles. Measurements of the efficiency of phosphorus smokes showed similar effects of humidity and temperature.

METHOD OF IGNITION

The B. M. smoke mixture may be ignited in several ways, but the most simple and fool-proof consists in using a train of preheating agents. The operation and construction of the smoke device in question usually determine the sequence of this train. Generally a delay is convenient between the ignition and the burst of smoke, in order that the operator may get away. The ignition may be caused by the firing of a cap, which starts the time fuse, which in turn ignites a capsule containing a mixture of potassium permanganate and reduced iron. The temperature reached by the oxidation of the reduced iron is sufficient to melt through the capsule and ignite the main B. M. mixture below. A starting mixture of reduced iron and potas-

sium nitrate functions as satisfactorily but possesses two disadvantages: it is not so stable under surveillance tests, and its reaction liberates gaseous products, often with explosive violence and the consequent rupture of the entire container.

CONCLUSION

The B. M. mixture with certain modifications in proportions has been used in grenades, smoke candles, Stokes bombs, Livens projectiles, smoke boxes, and various signal devices. It possesses greater possibilities than phosphorus, and it is possible that it might have displaced phosphorus as the most important smoke producer, if the war had continued. Several suggestions for its use in peace time have been made, but no active development is under way.

Dr. Martin Fischer Tells of European Trip

Dr. Martin Fischer, professor of physiology at the University of Cincinnati, who returned from Europe early in March, gave a highly interesting account of his impressions of conditions in the countries which he visited, at a meeting of the Cincinnati Section of the AMERICAN CHEMICAL SOCIETY, held March 9, in the Chemical Lecture Hall of the University of Cincinnati.

Dr. Fischer had given a series of lectures on colloids at the University of Amsterdam, by invitation, and in addition to his trip to Holland he had also visited parts of England and Germany.

He was impressed with the apparent absence of feeling regarding the late war in both the neutral and warring countries. The people seem anxious to forget all about the war and turn their attention to the problems of reconstruction. There is a marked feeling of friendliness toward the scientific men of foreign countries, and American men of science are particularly popular. They are known abroad by their works.

A change in the general attitude of people toward things of material advantage was observed by Dr. Fischer. People belonging to the educated group, including teachers, physicians, and scientists in general, seem to have been hit hardest by the change of things since pre-war days.

In Holland there are many distinguished scientists who are sometimes classified by Americans as natives of other countries, because of the fact that their articles are published in English, French, or German journals and also because they write their scientific papers in French, English, or German rather than in Dutch.

Dr. Fischer ascribed the splendid development of the Dutch people to the fact that there is keen competition among them at all times. A nation of seven million people confined to a comparatively small area can make as heavy an impress upon the world in general as the Dutch have made, only because of keen competition.

Dr. Fischer concluded his address with a plea for greater work and effort on the part of the American chemist in helping to conserve our natural resources and in developing our man power through the accomplishment of difficult tasks. He called attention to the laws of biology which underlie all human progress, and cited examples of the rise and fall of nations due to the workings of these laws. If we are to develop our brain power we must use our brains, and if we want to keep alive the strong men of our nation we must give them difficult and extensive work to do.

Lectures at the College of the City of New York

Announcement is made of a series of lectures to be held under the auspices of the City College Chemical Society. The lectures, to be given at 4.30 p. m. in the Doremus Lecture Theatre, are as follows:

- MR. ELLWOOD HENDRICK, "Beyond the Laboratory," March 7.
- DR. MARSTON TAYLOR BOGERT, Professor of Chemistry, Columbia University, "The Service of the Synthetic Dye Industry to the State," March 15.
- DR. CHARLES H. MACDOWELL, President, Armour Chemical Co., "The Trial of the Chemist in the Packing Industry," March 23.
- MR. ERNEST M. SYMMES, Hercules Powder Co., "Explosives in War and Peace," April 8.
- DR. DANIEL D. JACKSON, Professor of Chemical Engineering, Columbia University, "Chemical Evolution," April 14.

RESEARCH PROBLEMS IN COLLOID CHEMISTRY¹

By Wilder D. Bancroft

CORNELL UNIVERSITY, ITHACA, N. Y.

(Concluded)

GELATINOUS PRECIPITATES

(153) WHAT CONSTITUTES A GELATINOUS PRECIPITATE?—No one has any difficulty in recognizing a gelatinous precipitate, but we are not at all clear as to what gives an inorganic gelatinous precipitate these properties. In the case of gelatinous ferric oxide and silica, there is every reason to suppose that none of the water is combined to form a definite chemical compound. It may be that the rouge or the sand is precipitated as a supercooled liquid which is in itself viscous and gelatinous. If one objects to the distinctly arbitrary assumption that we have viscous liquids and water in the gelatinous precipitates, one alternative is to assume that solid particles and water behave like a gelatinous precipitate when the solid particles are sufficiently fine and provided they adsorb water sufficiently strongly. This is apparently what Zsigmondy² does; but he does not show why this should be so. Another alternative is to assume that the adsorbed ion makes the surface viscous. In the case of an emulsion this does happen. We may have drops of oil coated with a soap film and these may coalesce sufficiently to form a gelatinous mass. This is not helpful because the soap is gelatinous in itself. It is possible, however, that there is an intermediate stage between that of peptization and that of irreversible coagulation, where there may be a surface which is gelatinous in its properties. While something of this sort may happen, it has not been shown to take place. The real test would be to make a gelatinous gold precipitate without any protecting colloid. Until something of this sort has been done, or until we know why it cannot be done³ we must admit that we know very little in regard to what constitutes a gelatinous precipitate. A possible explanation with ferric oxide is that we have grains of oxide with a gelatinous film of instable ferric hydroxide adsorbed on the surface and stabilized thereby. This would not be inconsistent with the vapor pressure data because those show only that ferric hydroxide does not exist in mass under the conditions of the experiment. We know that sand can be converted into gelatinous silicic acid if ground sufficiently fine and that clay particles have a gelatinous coating. The difficulty is that this explanation does not help us in the case of barium sulfate, and either we must explain all gelatinous precipitates in the same way or we must divide them into groups and be able to distinguish between the groups.

(154) CRITICAL COMPARISON OF THE PROPERTIES OF STANNIC AND METASTANNIC ACIDS, TUNGSTIC AND METATUNGSTIC ACIDS, ETC.—There is apparently no place where one can find a clear statement of the exact difference between stannic and metastannic acids, for instance. An exhaustive monograph on the gelatinous oxides is needed very much.

(155) CHARACTERISTICS OF PRECIPITATED SULFUR—Odén⁴ found that the physical properties of sulfur precipitated from colloidal solution varied very markedly with the electrolyte used for precipitation. It came down as a hard precipitate with potassium salts, fine-grained with copper sulfate, plastic with barium salts, fluid with hydrochloric acid, and slimy with other salts. This work should be repeated and the reasons for these differences formulated.

(156) WHAT IS THE DIFFERENCE BETWEEN A FILM OR FILAMENT COMPOSED OF A VISCOUS LIQUID AND ONE COMPOSED OF

PARTIALLY COALESCED VISCOUS DROPS?—A film composed of partially coalesced viscous drops will have holes in it, while a liquid film will not. We need a discussion of the differences in properties, if any, of the two types of films, together with methods of distinguishing between them. The collodion ultrafilters are evidently sieves and a copper ferrocyanide membrane is probably a liquid film,¹ and we know that some of the properties of a copper ferrocyanide membrane can be duplicated with a liquid film. What is a rubber membrane and why?

JELLIES

(157) JELLIES IN NONAQUEOUS SOLVENTS—The formation of jellies in organic liquids should be studied because at present practically all our quantitative data are on aqueous jellies. Excellent jellies can be formed with soap in mineral oils. Pyroxylin solutions evaporate to jellies. Baskerville has patented the addition of 90 cc. alcohol to 10 cc. saturated calcium acetate solution, this procedure giving him an excellent "solid" alcohol.

(158) THE THEORY OF THE FORMATION OF HYDROUS OXIDE JELLIES AND THE EFFECT OF CERTAIN SALTS ON THEIR FORMATION AND PERMANENCY—There is no satisfactory theory of jellies. The most familiar hydrous oxide jellies are prepared by adding alkali to a salt until the precipitate formed is dissolved and allowing the solution to stand for a time. It has been found² that the presence of an excess of alkali and of certain salts has a deleterious effect on the formation and stability of jellies, while the presence of other salts seems to favor the formation. It is suggested that a jelly results when a highly hydrous oxide agglomerates from a colloidal solution. It may be possible to trace the effect of hydroxyl-ion concentration and the influence of certain salts to the varying agglomerating and stabilizing action of various ions on the colloidal oxide.³ Another form of the same problem which calls for more systematic study is the production of jellies by dialyzing⁴ out the peptizing agent.

(159) LIQUEFACTION OF A SODIUM STEARATE JELLY—Since a one per cent sodium stearate jelly must owe its rigidity to its structure, it ought to be possible to liquefy it by picking at it until it was disintegrated. Similar experiments should be tried with all sorts of jellies.

(160) THEORY OF SWELLING OF JELLIES—We have no satisfactory theory of the swelling of jellies. For instance, Arisz⁵ finds that at 20° a 0.5 per cent gelatin jelly disintegrates completely in water, a 10 per cent jelly goes to a 2 per cent jelly in 4 days, a 20 per cent jelly to a 6 per cent one, a 50 per cent jelly to a 16 per cent one, and an 80 per cent jelly to a 20 per cent one. Although the 20 per cent jelly will take up enough water so that its composition is equal to that of a 10 per cent jelly, the two do not then behave alike. The jelly which has swelled until its composition is 10 per cent will not then take up so much water in a reasonable time as a jelly which is made up at 10 per cent. This shows that there is probably a difference in structure and in the way in which the water is held, although Sheppard considers that these phenomena are due to changes in the shape of the mass and to a consequent unequal distribution of water. Until we have some satisfactory theory to account for this difference in behavior, all experiments on the swelling of gelatin

¹ This is disputed by Tinker, *Proc. Roy. Soc.* **92A** (1916), 357; **93A** (1917), 268.

² Cf. Bunce and Finch, *J. Phys. Chem.*, **17** (1913), 769; **18** (1914), 26; Nagel, *Ibid.*, **19** (1916), 331.

³ Weiser, *J. Phys. Chem.*, **24** (1920), 277.

⁴ Holmes and Arnold, *J. Am. Chem. Soc.*, **40** (1918), 1014; Holmes and Fall, *Ibid.*, **41** (1919), 763.

⁵ *Kolloidchem. Beihefte*, **7** (1915), 1.

¹ Received November 5, 1920.

² "Kolloidchemie," **1912**, 149.

³ It has been suggested that gold does not adsorb water sufficiently strongly to give a gelatinous precipitate.

⁴ "Der kolloide Schwefel," **1912**, 134, 157.

jellies in solutions of salts, acids, and bases are likely to be misleading, because one does not know to what extent the electrolytes are causing a change in structure. That a change in structure takes place even with water is shown by the experiments of Arisz on intermittent soaking. If two identical gelatin jellies are placed in water and one is kept in the water 6 days, while the other is in the water only on the first, fifth, and sixth days, the amount of swelling will be the same in the two cases, within the limits of experimental error. While the partially swollen jelly is out of the water, some change in structure takes place, such that it takes up water so much more rapidly than the other that the total swelling is the same in the two cases, although one jelly was soaked twice as long as the other.

(161) WILL DRIED GELATIN JELLIES BECOME IDENTICAL ON LONG STANDING?—If dried gelatin is placed in cold water it swells a good deal and may take up ten times its weight of water; but there are no experiments to show that it would ever go up, say, to an 8 per cent jelly. On the other hand, it is possible to start with an 8 per cent jelly and dry it to a 96 per cent jelly, after which it will take up water rapidly to an 8 per cent jelly. This means that the structure of the gelatin plays an important part in the rate of swelling. This is confirmed by some unpublished preliminary results by Mr. Cartledge. Gelatin jellies were made up containing 8, 16, 24, and 32 per cent of gelatin. These were all dried at room temperature to about 96 per cent concentration. When water was added, each swelled rapidly to the original concentration and then took up water slowly. If these results are accurate, it means that the four 96 per cent jellies were all different, and that the 8 per cent gelatin did not become like the 16 per cent, 24 per cent, or 32 per cent gelatin while being dried. If the different 96 per cent jellies were held long enough at some temperature below the point of obvious liquefaction, they should become identical. This ought to be tested.

(162) SYNERESIS OF JELLIES—In the case of some inorganic jellies, the presence of certain ions seems to be necessary either to ensure sufficiently slow precipitation or to prevent contraction. To get chromic oxide jellies,¹ acetate or sulfate must be present. With cupric oxide jellies² a small amount of sulfate is necessary. The theory of this should be worked out with special application to starch and gluten jellies because of its probable importance in connection with stale bread.³

(163) STRUCTURE OF COPPER FERROCYANIDE JELLIES—It is probable that it would be possible to make a copper ferrocyanide jelly. If that were done in a sugar solution and the jelly placed in water, the jelly might be expected to swell and disintegrate if the sugar solution were internal phase.⁴ If such a jelly were allowed to stand, it would be interesting to know whether syneresis would cause the exudation of pure water or of a sugar solution.

(164) CRYSTALLIZATION IN GELATIN JELLIES—If gelatin jellies of different concentrations were made up with saturated solutions of suitable salts, and were then dried, it ought to be possible to tell something about the structure of the gelatin jellies from the resulting structure of the crystals. If the jellies have a sponge structure, the salt might reasonably be expected to crystallize in a more or less coherent, feathery mass. If the jellies have a honeycomb structure, one would expect to get granular masses. It would be essential to take salts which tended to crystallize in branching needles. If the gelatin could be hardened with tannin or formaldehyde, the results might be even more instructive.

(165) STUDY OF RHYTHMIC BANDING—Holmes⁵ has shown that colloidal gold gives three colored bands—red, purple, and blue—

before repeating. This has not been considered in any theory of rhythmic banding and yet it seems to offer an important clue.

(166) REPETITION OF VON SCHROEDER'S EXPERIMENTS—In Ostwald's laboratory von Schroeder¹ claimed to have found that a gelatin jelly which is in equilibrium with saturated water vapor will take up more water when placed in liquid water. Wolff and Buchner² claim that von Schroeder's results were due to experimental error, while Washburn³ apparently believes that they were right, but that the effect is due to gravity. Under the circumstances the experiments ought to be repeated. It might be a good plan to do similar experiments with rubber and an organic liquid.

(167) EQUILIBRIUM PRESSURES FOR RUBBER, GELATIN, ETC., WHEN THE AMOUNT OF LIQUID IS VERY SMALL—Posnjak⁴ has made some experiments on the amount of water with which gelatin is in equilibrium under different pressures and he has also studied the corresponding behavior of raw Para rubber in different organic liquids. The most concentrated solutions which he studied contained 0.92 g. water per gram of gelatin and 2.09 g. benzene per gram of rubber, and his highest pressure was about 5 atmospheres. These experiments should be extended to cover the more interesting range of the initial swelling.

(168) CLOUDING OF A SILICA GEL—When a silica gel dries, it clouds at the center owing to the appearance of air bubbles, the water apparently evaporating from the center instead of from the outside. Zsigmondy⁵ suggests that there is a tendency for the water to rise to the surface of the capillaries and that the dissolved air comes out at the center. The phenomenon should be duplicated and studied, using a capillary tube closed at one end.

(169) HARDENING OF GELATIN BY CHROMIC SULFATE—The experiments of Lumière and Seyewetz⁶ indicate that gelatin decomposes chromic sulfate, adsorbing the chromic oxide very strongly and the sulfuric acid less strongly. This simultaneous adsorption of a free base and a free acid is an unexpected phenomenon and calls for careful study.

(170) STUDY OF CALCIUM SUCRATES—In view of the way in which sugar solutions promote the formation of colloidal solutions of the heavy metal hydroxides, the question arises whether there are any calcium sucates. Cameron and Patten⁷ did not obtain any as solid phases in their work. The work on the calcium sucates⁸ should be repeated, and a study should also be made of the conditions under which solutions set to a jelly.

(171) ACTION OF LIME ON OPTICAL ROTATION OF SUGAR—It is stated⁹ that the addition of lime water to a sugar solution diminishes the rotary power of the solution though according to no apparent law. Acetic acid restores the rotary power. This should be discussed with reference to the existence or non-existence of the calcium sucates, No. 170.

(172) CHLORAL HYDRATE AND CAMPHOR—According to Brown,¹⁰ a rise of temperature is observed if chloral hydrate and camphor are rubbed together in a mortar, and a sirup is obtained which is neutral to test papers and does not give a precipitate with silver nitrate. On treatment with distilled water, it hardens to a translucent white solid. The chloral hydrate can be dissolved, leaving the camphor in crystalline grains. This should be investigated for itself and also for its bearing on the formation of celluloid.

¹ *Z. physik. Chem.*, **45** (1903), 109.

² *Ibid.*, **89** (1915), 271.

³ *J. Am. Ceram. Soc.*, **1** (1918), 25.

⁴ *Kolloidchem. Beihefte*, **3** (1912), 417.

⁵ *"Kolloidchemie,"* **1912**, 160.

⁶ Bancroft, *J. Phys. Chem.*, **24** (1920), 25.

⁷ *J. Phys. Chem.*, **15** (1911), 67.

⁸ Horsin-Deon, *J. Chem. Soc.*, **25** (1872), 810; **26** (1873), 612; Puscher, *Ibid.*, **26** (1873), 306; Carles, *Ibid.*, **27** (1874), 422; Latour, *Ibid.*, **27** (1874), 423; Loiseau, *Ibid.*, **46** (1884), 419; Petit, *Ibid.*, **64**, I (1893), 451; Svedberg, "Die Herstellung kolloider Lösungen," **1909**, 305.

⁹ Desor, *J. Chem. Soc.*, **38** (1880), 834.

¹⁰ *J. Chem. Soc.*, **27** (1874), 723.

¹ Bunce and Finch, *J. Phys. Chem.*, **17** (1913), 269; Nagel, *Ibid.*, **19** (1915), 331.

² Finch, *Ibid.*, **18** (1914), 26.

³ Wo. Ostwald, *Z. Kolloidchem.*, **25** (1919), 37.

⁴ Cf. Tinker, *Proc. Roy. Soc.*, **92A** (1917), 268.

⁵ *J. Am. Chem. Soc.*, **40** (1918), 1187.

EMULSIONS

(173) ADSORPTION OF GELATIN BY OIL—Winkelblech¹ has shown that gelatin concentrates at the dineric interface when organic liquids are shaken with water. Holmes and Child² find that with kerosene-in-water emulsions, with gelatin as emulsifying agent, there is apparently no adsorption of gelatin at the oil-water interface.

Had there been any concentration by adsorption around the oil droplets, the liquid below the cream should have been poorer in gelatin than the original solution. To test this we withdrew 5 cc. from the lower layer and analyzed for nitrogen by the Kjeldahl method. Even with the most dilute gelatins, analysis showed a loss of only 0.008 g. which meant nothing since in making emulsions we did not attempt accuracy beyond one part in a thousand.

The discrepancy between the two sets of measurements should be cleared up.

(174) EFFECT OF CONCENTRATION ON TYPE OF EMULSION—Bhatnagar³ has used a conductivity method as a means of determining whether an emulsion is oil-in-water or water-in-oil. He seems to have found that with potassium oleate as emulsifying agent, the emulsion changed from the oil-in-water type to water-in-oil when the oil concentration became high enough. This contradicts the most careful measurements that have been made hitherto and raises the question of the accuracy of Bhatnagar's measurements. He did not work with a constant amount of potassium oleate as he should have done. Instead, he used a constant amount of potassium hydroxide and a varying amount of oleic acid, the concentration of oleic acid in the oil being constant. "The bottles were shaken for a constant time after each addition in a powerful mechanical shaker, and the total time of shaking was kept constant to ensure identical conditions." Working in this way it would be practically impossible to get the high concentrations of oil in water,⁴ and consequently the most that his experiments could show would be the limiting efficiency of the shaker. This seems to have been the case for he says:

It is found that the water-in-oil type with kerosene oil is very unstable. The emulsion shows no conductivity for a minute or two, and then it gradually rises until it indicates its previous conductivity. The drops of water, as they de-emulsify, are visible, and are seen constantly falling to the bottom, until the emulsion undergoes complete disintegration.

In addition to these sources of error, there is a possibility of a special error in the case of olive oil. Olive oil is an indefinite substance and may contain varying amounts of stearin, presumably in colloidal solution. When working with small amounts of soap and large amounts of olive oil, it is possible that a reversal of type may have actually occurred because of the presence of an emulsifying agent in the olive oil. It is evidently necessary that these experiments should be repeated making use of the best technique.

(175) EMULSIFYING AGENTS FORMING COLLOIDAL SOLUTIONS IN BOTH LIQUIDS—In many cases emulsifying agents are used technically which form colloidal solutions both in the oil phase and the water phase, though more readily in one than in the other. It is appreciably easier to form emulsions quickly under these conditions than when the emulsifying agent forms a colloidal solution in only one of the liquids. The theory of this has not been worked out. It is quite possible that in these cases the amount of emulsifying agent may have to be larger than in the normal cases. For instance, Winkelblech⁵ was not able to coagulate gelatin in water by shaking with ether, while Miller and McPherson⁶ found that arsenious sulfide dis-

tributes itself between the ether and the water layer, though forming a colloidal solution in both.

(176) MAYONNAISE—Briggs¹ has shown that intermittent shaking is much more effective than continuous shaking in producing emulsions. These experiments throw some light on the making of mayonnaise. Since mayonnaise is essentially an emulsion of oil in water (vinegar) with egg as the emulsifying agent, it ought to behave like any other emulsion, and so it does for the experts in the Departments of Home Economics. They can add the ingredients in any order, all at once or in separate portions, hot or cold, and the mayonnaise always comes. On the other hand, these same experts do not train their pupils so that these latter can make mayonnaise every time. It seems certain that the experts do something or other unconsciously which they consequently do not tell to their pupils. Probably the expert is so sure of the result that she works leisurely without being hurried or flurried, and is practically doing intermittent stirring. The person who is not an expert and who is uncertain of the outcome probably goes at her task so vigorously as to defeat her object in many cases. While this explanation has not been tested, one expert said that she had found that if the materials were beaten well together, and then allowed to stand for a moment or two, a couple of swishes would make the mayonnaise. I have been told that Béarnaise sauce is an emulsion of melted butter in tarragon vinegar without any egg, and that it is very easy to make. If this is so, tarragon vinegar must contain a good deal more of some emulsifying material, probably a tannin, than ordinary vinegar. A study should be made of the different recipes for making mayonnaise and the results accounted for.

(177) SAPONIFICATION OF FATS WITH LIME—When caustic soda is used to saponify fats, it is necessary to use at least the theoretical amount if practically complete hydrolysis is to be obtained. When working with lime in an autoclave at 12 atmospheres pressure (corresponding to a temperature of 195°), it is possible to cut the amount of lime down to about one-tenth of that necessary to neutralize all the acid in the fat, 0.1 per cent of lime causing practically complete hydrolysis.² It seems probable that the real hydrolyzing agent is water, and that the lime is important because the calcium soap which is formed causes the water to emulsify in the fat instead of the fat in the oil. This is the more probable because magnesia and zinc oxide act like lime. There is no direct experimental proof, however, of this explanation of the action of lime.

FOAM

(178) STUDY OF BUBBLES—While a great deal of work has been done on soap bubbles, it has been done without taking into account the fact that soap forms a colloidal solution with water and that the hydrolysis of the soap will change with the varying thickness of the film. It is practically certain that a study of the existing data from the viewpoint of the colloid chemist would lead to the solution of some of the problems involved.

(179) COLLOIDAL GAS BUBBLES—It is generally believed that natural mineral waters lose their gas more slowly than artificially charged waters. If this is true, it must be because of colloidal material in the natural waters which keeps the bubbles very small.³ This should be duplicated experimentally.

(180) BUBBLE FLOTATION OF CALCIUM CARBONATE, COLLOIDAL GOLD, AND WHITE LEAD—We know that calcium carbonate goes into the oil-water interface,⁴ while calcium sulfate does not. We also know that colloidal gold⁵ goes into the oil-water interface.

¹ *Z. angew. Chem.*, **19** (1906), 1953.

² *J. Am. Chem. Soc.*, **42** (1920), 2049.

³ *J. Chem. Soc.*, **117** (1920), 544.

⁴ Briggs, *J. Phys. Chem.*, **24** (1920), 120.

⁵ *Z. angew. Chem.*, **18** (1906), 1953.

⁶ *J. Phys. Chem.*, **12** (1908), 706.

¹ *J. Phys. Chem.*, **24** (1920), 120.

² Thorpe, "Dictionary of Applied Chemistry," **4** (1913), 639.

³ Wolfgang Ostwald, *Z. Kolloidchem.*, **25** (1919), 41.

⁴ Hofmann, *Z. physik. Chem.*, **83** (1913), 385; Bancroft, *J. Phys. Chem.*, **19** (1915), 286.

⁵ Reinders, *Z. Kolloidchem.*, **13** (1915), 325.

More to complete the record than anything else, it should be shown that both these substances can be floated up by the bubble method of ore flotation. The calcium carbonate experiment is important in its bearing on the behavior of calcareous ores.

Since white lead¹ is wetted preferentially by linseed oil and zinc oxide² by water, a study should be made of bubble separation of these two, paying especial attention to the effect of the relative sizes of grain.

(181) BUBBLE FLOTATION OF SEWAGE—Biltz and Kröhnke³ tried to remove the colloidal matter from sewage by shaking with organic liquids, but were not successful because only about 30 per cent extraction was obtained. This is really an application of the Elmore bulk oil method. Since this has been superseded in the mining world by bubble flotation, it seems desirable to try bubble flotation with sewage to see whether an improvement in yield can be obtained and, if so, how great a one. A point which Biltz and Kröhnke did not know is that addition of any salt which decreases the stability of the colloidal solution will increase the amount of extraction.⁴ The process might be applicable to milk wastes.

(182) STABILIZATION OF FOAM—To get a foam the only essential is that there shall be a distinct surface film, in other words, that the concentration in the surface layer shall differ perceptibly from that in the mass of the liquid. All true solutions will, therefore, foam if there is a marked change of surface tension with change of concentration, regardless of whether the surface tension increases or decreases. All colloidal solutions will foam if the colloid concentrates in the interface or if it is driven away from the interface. To get a fairly permanent foam the surface film must either be sufficiently viscous in itself or must be stabilized in some way. This can be done by introducing a solid powder into the interface.

Solutions of aqueous alcohol, acetic acid, sodium chloride and sulfuric acid all foam when shaken; but the foam is instable. Soap solutions foam when shaken and the foam is, or may be, quite stable owing to the viscosity of the soap film. With saponin the surface film is even more stable. If we add to aqueous alcohol some substance like lycopodium powder which goes into the interface, we get a stabilized foam. We can do the same thing with aqueous acetic acid by adding lampblack. The presence of enough of a finely divided solid in the interface will make the film so viscous that the foam will be quite stable. Grease will help stabilize a foam in some cases and it has been claimed erroneously that the foaming of sulfuric acid solutions is due to grease.⁵

In 1857, Gladstone⁶ pointed out that aqueous solutions of organic substances are apt to froth, and he cited beer as a then familiar instance. He did not realize, however, that it was the colloidal matter in the beer which caused the frothing. It has been shown by Zeidler and Nauck⁷ that removing the albumoses from beer destroys the foaming. Gladstone showed, however, that the dissolved air was not essential to the frothing. If this were pumped out in a vacuum, the liquid frothed freely when shaken with air. Gladstone states that aqueous solutions of the acetates of iron, copper, lead, and other metals froth readily, especially the ferric acetate solution. As we know, this is the one which hydrolyzes most readily, and the frothing is due undoubtedly to the combined effect of the acetic acid and the hydrous ferric oxide.

There has been no systematic study as yet of the stabilization of foam. The armor-plated bubbles of the Minerals Separation Company's process consist of air bubbles, with an

oil film round them, in water and stabilized by adsorbed ore particles. When these bubbles rise to the top, they form a very stable froth. The Foamite process for fighting fire consists in the production of a froth of carbon dioxide bubbles made stable by a film of hydrous alumina and another substance which is reported to be licorice or something of that sort. The technical development of the subject has gone well ahead of the scientific side, and it is desirable to restore the balance.

(183) DESTRUCTION OF FOAMS AND EMULSIONS—There has been a good deal of scientific work done recently on the stabilization of emulsions and foams; but the destruction of emulsions and foams may be quite as important technically. A number of methods are known already and the oil companies probably have a large amount of unpublished information, especially on the cracking of emulsions; but no systematic study of the subject has been made. There is no certainty that better methods may not be devised than any we now have, and there is no way at present of telling in advance which of the known methods is the best in any particular case.

NONAQUEOUS COLLOIDS

(184) STUDY OF NONAQUEOUS COLLOIDS—Most of the research work on colloids has been concerned with aqueous sols and gels. This work should be paralleled by studies of the behavior of colloidal solutions in alcohols, esters, hydrocarbons, chloroform, acetone, ether, carbon tetrachloride, fats, waxes, melted sulfur, camphor, melted salts, etc. While peptization or stabilization by ions is relatively unimportant in most of the cases, it may play an important part with melted salts, and may be a minor factor with certain other nonaqueous solvents. The study of the other types of sols is important in itself and will probably throw light on the behavior of some of the aqueous sols.

The chemistry of the cellulose esters is a fruitful field for research in colloid chemistry. These substances are peptized by a number of liquids (so-called solvents), and can then be converted into jellies, films, filaments, etc.

(185) BEHAVIOR OF MIXED COLLOIDS IN NONAQUEOUS SOLVENTS—When a mixture of hydrous chromic oxide and hydrous ferric oxide is treated with caustic soda solution, the mixture is peptized, giving an apparently clear green sol in case the hydrous chromic oxide is present in sufficient excess, the hydrous chromic oxide peptizing the ferric oxide.¹ When the hydrous ferric oxide is in excess, there is no peptization at all and the sodium hydroxide solution remains colorless because the hydrous ferric oxide adsorbs the chromic oxide and keeps it from being peptized. People believed that they had pure oxycellulose because the product did not behave like cellulose, and yet the evidence is very strong that nobody has ever prepared pure oxycellulose.² It seems probable that there are nothing like the number of cellulose nitrates which the literature revels in and that people are dealing with mixtures of perhaps not over three cellulose nitrates which are peptized very differently and have different apparent properties depending on the relative amounts and on the way in which they are adsorbed. Preliminary experiments, made before the war by Mr. M. W. Bray, indicated that this was the case.

(186) BLACK PHOSPHORUS—The literature on black phosphorus is very confused³ and the subject is not mentioned in Thorpe's "Dictionary of Applied Chemistry." Apparently mercury, arsenic, etc., can form colloidal solutions in phosphorus, and it would probably be interesting to study these.

FOG

(187) DRY FOG—Dense fogs have been noticed around London when the humidity was only 50 to 80 per cent. Frankland⁴ believes that this is due to films of oil from coal smoke coating

¹ Holley, "Lead and Zinc Pigments," 1909, 71.

² Cruickshank Smith, "The Manufacture of Paint," 1915, 92, 103.

³ Z. angew. Chem., 20 (1907), 883.

⁴ Briggs, J. Phys. Chem., 19 (1915), 210.

⁵ Lang, Ber., 18 (1885), 1391.

⁶ Phil. Mag., [4] 14 (1857), 314.

⁷ J. Soc. Chem. Ind., 20 (1909), 260.

¹ Nagel, J. Phys. Chem., 19 (1915), 331.

² Bancroft, Ibid., 19 (1915), 159.

³ See Dammer, "Handbuch der anorganischen Chemie," 2, I (1894), 95.

⁴ Proc. Roy. Soc., 28 (1879), 238.

the drops of water and retarding the evaporation. While this explanation is probably true, we do not know under what conditions a fog of oil and water gives drops of water coated with oil or drops of oil coated with water. From our experience with emulsions, it seems that it should be possible to make water-in-oil fogs and oil-in-water fogs; but this has never been studied. If we consider the case solely as oil, water, and air, only one type will be possible, just as only one type is possible in an emulsion with a given emulsifying agent. If we add a fourth component, I see no reason why we may not get a reversal. In view of the fact that lampblack enables us to emulsify water in oil,¹ a smoky atmosphere might well be conducive to the production of dry fogs.

(188) SYNTHETIC THUNDER STORMS—Simpson² has developed a theory of thunder storms which seems to be the best available, though it is by no means accepted universally. He assumes the existence in the center of the storm of a rapidly ascending current of air which spreads out and loses speed above a certain height. Large rain drops will fall through this air current until they reach a point where they are broken into smaller drops, and are then carried to the upper and colder levels where they grow again and repeat the cycle. When the drops break up they become charged positively, while the negative ions are carried up more rapidly by the air and are finally caught by cloud particles at some higher level. Simpson satisfied himself that the electricity generated by the breaking up of the falling drops might easily account for the gradient of 30,000 volts per centimeter necessary for lightning. If we could make a synthetic thunder storm in the laboratory by means of a blower, it would enable us to test Simpson's theory in a way that cannot be done now, and it would probably be of great interest in other meteorological problems. If we change from flashes of lightning a mile or so long to flashes an inch long, the other dimensions of the thunder storm would be decreased considerably, though we do not know to what extent. It is a problem in mathematical physics to determine approximately the minimum theoretical size of a thunder storm.

(189) THEORY OF SMOKE PRECIPITATION WITH ALTERNATING CURRENT—Lodge³ tried the effect of electrification on a mass of smoke. With potentials of one hundred volts very little effect could be detected. When the potential rose to a few thousand volts and a brush discharge began to be possible, the smoke agglomerated and settled very rapidly. The theory of this has never been worked out. In ordinary smokes about 30 per cent of the particles are charged electrically. It may be that the alternating current reverses the sign of the charge periodically and that the particles agglomerate when they are electrically neutral, or it may be that it causes the charged particles to collide with the uncharged ones. In connection with this it would be interesting to determine the effect of a high-voltage alternating current on the stability of a suspension in a practically non-conducting liquid.

(190) DO COARSE AND FINE POWDERS ATTRACT OR REPEL EACH OTHER WHEN BOTH HAVE THE SAME ELECTRICAL CHARGE?—Two liquid drops of the same size repel each other if they have equal electrical charges of the same sign. When two drops bearing unequal charges, or two unequal drops bearing equal charges, are brought closely enough together, there are immensely strong, increasing forces of attraction between them, and coalescence will surely take place if the resulting drop is not as large as to be unstable.⁴ Nobody seems to have discussed whether two electrically charged solid particles, smoke for in-

stance, may attract each other under suitable conditions, even though the sign of the charge on the particles is the same.

PRECIPITATION OF SOLID

(191) FORMATION OF MIRRORS—The formation of a metallic mirror involves the precipitation of the metal in a very finely crystalline form. It is, therefore, a problem in colloid chemistry, and the literature on the subject¹ should be gone over and presented from this point of view.

(192) STUDY OF FILAMENTOUS PRECIPITATIONS—There is a certain amount of literature on filamentous silver,² mossy copper,³ filamentous potassium chloride,⁴ and on silver chloride growths⁵ with silver, sodium chloride, and gelatin; but there is no adequate discussion on the subject from the point of view of a colloid chemist.

(193) COLORS OF SILVER SOLS IN DIFFERENT VESSELS—If hydrogen is passed into a saturated aqueous solution of silver oxide containing an excess of the solid salt, silver precipitates to some extent as crystals and in part as colloidal silver.⁶ The form in which the metal comes down depends on the nature of the containing vessel. In a platinum vessel no hydrosol is formed, and all the silver precipitates in a crystalline form on the walls of the vessel. In vessels of quartz and of ordinary glass, the colloidal silver is yellowish brown by transmitted light, while it comes down red to blue in a flask made of Jena glass. The ratio of silver hydrosol to ordinary silver is greater in the Jena glass vessel than in the other two. At first sight one would expect this difference in behavior to be due to differences in material dissolved from the walls, but this is not the case. Kohlschütter allowed water to stand in an ordinary glass flask for a while and then poured it into the Jena glass flask. The reduction product was red. When water which had stood in a Jena glass flask was poured into an ordinary flask or into a quartz one, the silver came down yellowish brown. The phenomenon is, therefore, connected with the presence and nature of the solid. The more plausible explanation is, as suggested by Kohlschütter, that the reaction concentrations are highest at the surface of the platinum and lowest at the surface of quartz and the ordinary glass, so that the silver comes down coarsest and most crystalline in platinum vessels and finest in quartz. This could be checked experimentally by determining the adsorbing power of platinum, quartz, and Jena glass for silver oxide and for colloidal silver. It is probable that the adsorption is greatest with platinum and least with quartz. This behavior of the silver may be connected with the fact that it is easier to get a yellow stain⁷ of silver on a potash-lime glass than on the hard glasses.

(194) SEDIMENTATION—Dewar⁸ states that if a glass rod is cooled to the temperature of liquid air and is then brought into the air of the room, moisture will condense on it as a sheet of ice. If the glass rod is electrified with a piece of silk, the ice forms as a forest of crystals and not as a sheet. The reason for this seems to be that the ice particles are themselves electrified and consequently precipitate as far from each other as possible. It is possible that something of this sort may play a part in determining the very different volumes which the same precipitate may occupy, depending upon the way in which it is precipitated.⁹

¹ Cf. Wadsworth, *Z. Instrumentenk.*, **15** (1895), 22; Neogi, *Z. anorg. Chem.*, **59** (1906), 213; Chattaway, *Proc. Roy. Soc.*, **80A** (1908), 88; Silverman and Neckerman, *Trans. Am. Ceram. Soc.*, **17** (1915), 505.

² Kohlschütter, *Z. Elektrochem.*, **14** (1908), 49; **18** (1912), 373, 419; *Ann.*, **387** (1912), 86; **390** (1912), 340; **398** (1913), 47; Phillips, *J. Chem. Soc.*, **72**, II (1897), 32.

³ Hutchings, *J. Chem. Soc.*, **32** (1877), 113.

⁴ Warrington, *Ibid.*, **8** (1856), 30.

⁵ Lüppo-Cramer, *Z. Kolloidchem.*, **9** (1911), 116.

⁶ Kohlschütter, *Ibid.*, **14** (1908), 49.

⁷ Rosenhain, "Glass Manufacture," **1908**, 185.

⁸ *Chem. News*, **97** (1908), 5.

⁹ Schulze, *Pogg. Ann.*, **129** (1866), 366.

¹ Schlaepfer, *J. Chem. Soc.*, **113** (1918), 522; Moore, *J. Am. Chem. Soc.*, **41** (1919), 940.

² *Phil. Trans.*, **209A** (1909), 379; Humphreys, *J. Frank. Inst.*, **179** (1914), 751; *Phys. Rev.*, **[2]** **6** (1915), 516.

³ *Phil. Mag.*, **[3]** **17** (1884), 214; *J. Soc. Chem. Ind.*, **5** (1886), 572.

⁴ Burton and Wiegand, *Phil. Mag.*, **[6]** **23** (1912), 148.

(195) MECHANISM OF THE ACTION OF COLLOIDAL ADDITION AGENTS IN THE ELECTRODEPOSITION OF METALS.—In order for a colloidal addition agent to function well, it must be carried to the cathode and be adsorbed by the precipitating metal in suitable amount to give the desired crystal size. Are the best results obtained with an addition agent which shows a strong preferential adsorption for the specific ion deposited, or is this both unnecessary and undesirable? A quantitative determination of the adsorption of lead ion, for instance, by a particularly good addition agent and by a comparatively poor one should be made. Quantitative determinations should also be made of the adsorption of various addition agents during the precipitation of colloidal metals.

(196) THE CAUSE OF THE HIGH RESULTS IN THE DETERMINATION OF ZINC BY THE ELECTROANALYTICAL METHOD.—In electroanalysis, zinc is precipitated from strongly alkaline solution and the results obtained are uniformly high. Under these conditions, the zinc is, at least in part, in colloidal solution as the hydrous oxide which gradually agglomerates and settles out on standing.¹ It is altogether possible that the high results are due to the separation of a part of this colloidal hydrous oxide during the analysis, thus contaminating the deposit. This could be determined by a careful quantitative investigation of the results under widely varying conditions.

GASES IN SOLIDS

(197) GLUTEN IN WHEAT.—Some wheat flours require admixture with other flours in order to ensure good bread. Work by Gortner, Henderson, and others indicates that the glutes are not chemically different and that the observed differences are due to salt content, hydrogen-ion concentration, etc. The problem is, therefore, one in colloid chemistry involving size and arrangement of aggregates, degree of hydration, etc. It might be possible to treat a flour with a so-called weak gluten so as to bring it more nearly up to standard. Anybody interested in this important problem should get in touch with Dr. H. E. Barnard, American Baking Institute, Minneapolis, Minn.

SOLIDS IN SOLIDS

(198) DETERMINATION OF PIGMENTS IN GLASSES AND GLAZES.—Our knowledge of the chemistry of colored glasses and glazes is extremely rudimentary.² This is due in part to the difficulty of manipulation and still more to the analytical difficulties. By working with the coloring oxides dispersed in alumina, it would be possible to work with a two-component system and thus simplify the analytical problem. Other oxides could be substituted for alumina and working with a borax or phosphate bead would be much easier than working with a regular glass.

(199) COLLOIDAL SILVER IN PRESENCE OF BISMUTH OXIDE.—In enamels the addition of silver carbonate and bismuth oxide gives an intense blue.³ One function of the bismuth oxide is to hold the silver to the body; but it must also cause a partial agglomeration of the silver because the lusters are blue to green instead of yellow to brown. Experiments should be tried in precipitating silver oxide with bismuth oxide and then reducing the silver oxide, so as to keep the laboratory experiments in close connection with the technical methods.

(200) ACTION OF ULTRAVIOLET LIGHT AND OF RADIUM ON GEMS.—The action of heat, ultraviolet light, and radium on the colors of gems is very interesting and opens up a broad field for research.⁴ Pale amethysts become darker when exposed to radium, while ultraviolet light has no effect. When heated to redness in hydrogen or oxygen, the pale amethysts become colorless, while they turn yellow if heated in ammonia. The decolorized

amethysts regain their color when treated with radium. Rose quartz is made colorless by ultraviolet light and blackish brown by radium. It is not changed when heated in ammonia. Smoky quartz loses its color when heated and radium brings it back, while hydrogen peroxide tends to make the color yellower. Colorless topaz is made yellow to orange by radium and is decolorized when heated. Ultraviolet light tends to change the orange produced by radium to lilac. Kunzite changes from lilac to green under the influence of radium and is changed back by ultraviolet light. It becomes colorless when heated to 400°, but exposure to radium brings back the blue-green color. Corundum occurs as blue, green, violet, yellow, and white sapphires and as ruby. The Oriental sapphire is said by Verneuil¹ to be colored by iron and titanium, while the clear sapphire is colored by iron only. Blue sapphires are changed to yellow or yellowish brown by radium, the blue-green sapphires to green, and the white sapphires to yellow. Violet sapphires become pure red and natural rubies lose any violet tinge. Artificial rubies and sapphires are not changed by exposure to radium, but their coloring matter is chromium or cobalt. Ultraviolet light makes yellow sapphires blue and violet ones more violet. Heating sapphires in air makes them colorless. Soddy has shown that colorless gold glass is turned to ruby by the action of radium emanation.²

The general result seems to be in all cases that heating makes the gems more nearly colorless and that the action of radium and of ultraviolet light is antagonistic. The only possible explanation seems to be that radium increases the dispersity of the colloidal particles, while ultraviolet light decreases it or vice versa. We know that β -rays increase the agglomeration of sulfur and that they change a selenium hydrosol into crystalline selenium. It should be possible to test this explanation on synthetic materials, using perhaps borate glasses. For instance, radium produces no change in pure chromic oxide but turns it brown when the chromic oxide is dissolved in borax. Ultraviolet light changes the brown to yellow, and when a chromium oxide borax glass is heated in ammonia it becomes pale. Alumina is not changed by radium but hydrous aluminium oxide sol is turned blue by it. If cases of this sort should be studied carefully it would probably give us the necessary data to straighten out the question of the colors of gems without any difficulty.

U. S. Army Examinations

A final competitive examination for appointment of second lieutenants in the Regular Army will be held beginning April 25, 1921. Among the vacancies to be filled are thirty-two in the Chemical Warfare Service.

Information as to the scope and details of the examination is contained in Army Regulations No. 605-5, which may be obtained by candidates at any military post or station. Applications should be submitted at once at any post or station, or at the headquarters of the department or corps area in which the candidate resides.

Institute for Research in Tropical America

Plans are under way for the organization of an Institute for Research in Tropical America for the promotion of exploration and research in the interest of natural science. The movement was inaugurated by the division of biology and agriculture of the National Research Council and will be primarily devoted to biological research to promote medicine, agriculture, forestry, fisheries, and general scientific development in Central and South America. Research stations for experimentation will be established in the countries investigated.

Medicinal Research on Animal Tissues

The municipal authorities of Paris have voted a fund for the establishment of a laboratory in connection with the city slaughter-house at La Villette for research into further medicinal uses for extractives of animal glands and tissues.

¹ Hantzsch, *Z. anorg. Chem.*, **30** (1902), 289; Fischer and Herz, *Ibid.*, **31** (1902), 352.

² Bancroft, *J. Phys. Chem.*, **23** (1919), 603.

³ Franchet, *Ann. chim. phys.*, [8] **9** (1906), 37.

⁴ Bancroft, *J. Phys. Chem.*, **23** (1919), 642.

¹ *Compt. rend.*, **151** (1910), 1053.

² Garnett, *Phil. Trans.*, **203A** (1904), 400.

SCIENTIFIC SOCIETIES

Rochester Ready for Chemical Cohorts

Special Correspondence to THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY by JOHN WALKER HARRINGTON

ROCHESTER, N. Y., MARCH 20—Tulips soon will blaze in the parks and spring burgeon in every square of Rochester. Surely the lines of those who are to attend the April meeting of the AMERICAN CHEMICAL SOCIETY will fall in pleasant places! Scarcely is the chill of March driven from the ground in the valley of the Genesee before Rochester becomes a smiling garden.

No more fitting place could have been chosen for the SOCIETY to renew its youth. Here it was that in 1891, before the organization had attained its national scope, its fifth general meeting was held, and again in 1913, it gathered here when it had reached the 7000 mark in membership. It is expected, judging from the returns received by the active local committees, that fully 2500 of the more than 15,000 members of the SOCIETY will be present when President Smith taps his gavel on the morning of April 26.

It is estimated that within a night's travel there are fully 9000 of our members. Rochester is easily accessible from New York, Boston, Philadelphia, Baltimore, and many other cities of the Atlantic seaboard. It can be reached readily from Chicago, Minneapolis, St. Louis, Cleveland, Cincinnati, and scores of other important communities. As an important railroad center, Rochester also offers special advantages in transportation to the large and flourishing sections of the SOCIETY on the Pacific Slope. The announcement that all members attending the Spring Meeting may, upon obtaining proper certifications, avail themselves of the fare and a half rate will also have a stimulating effect upon the attendance.

Delegations from the Middle West are likely to be unusually large. Dr. Gerald L. Wendt has issued a call in the *Chemical*

Bulletin, urging the membership of the nine sections around Chicago to join in a special train to Rochester. Mr. Herbert G. Sidebottom, secretary of the New York Section, has begun his campaign for a special car, or cars, and several other sections are planning either to come in reserved Pullmans, or to attend in large groups.

The veterans of the SOCIETY who knew Rochester 25 years ago will find that industrial chemistry has had much to do with her commercial advancement. Nearly 30,000 of her citizens, in a population of more than a quarter of a million, gain their livelihood from chemical industries or enterprises under chemical control. In Kodak Park alone there are, in round numbers, 6000 men and women employed. Since the war the industries of Rochester have made giant strides, for they have been instru-

mental in breaking the strangle hold of German monopoly in such commodities as optical glass and refined chemicals. Enormous quantities of chemical and other scientific apparatus are produced here, and Rochester is doing much toward the equipping of the laboratories of the universities and colleges, as well as those of research and industry.

If time permitted, Rochester could indeed make an exposition of the chemical industries within her borders. The Rochester Section, although it cannot arrange for exhibits on a large scale, is preparing a series of charts and graphs which will illustrate the importance of the community as a chemical headquarters, and will also show the relationship of the industrial chemistry practiced here to the country at large.

What Rochester does in preparing the chemists of the future for their life work is well visualized in the University of Rochester, under the able direction of its president, Dr. Rush Rhees. The department of chemistry, of which Dr. Victor John Chambers is the head, has well-maintained laboratories in which the student may not only obtain a general knowledge of chemistry but in which he may prepare himself for the career of chemical engineer. In Eastman Hall, which is dedicated to our science, are well-equipped laboratories, and one of its lecture rooms is frequently the meeting place of the Rochester Section.

The arrangements made by the indefatigable local committees will give full play to all the activities of the coming meeting—scientific and social.

Those who wish full opportunity to discuss the technical papers in academic calm will have it in the large and airy rooms of the Mechanics Institute at 55 South Plymouth Avenue, within a block of the official headquarters. The head of the department of chemistry there, Dr. J. Ernest Woodland, who is also chairman of the local Executive Committee, has arranged

that the various divisions and sections of the SOCIETY will have the entire use of the building during the Spring Meeting, as no classes will be held during that period. This will place equipment and apparatus of all kinds at the disposal of those who are reading papers, and will create that atmosphere of both pure and applied science which was a feature of the divisional meetings held last autumn at the University of Chicago. As all these gatherings are to be held under the same roof, it will be very easy for members to go from one division to another and to follow the papers in which they are especially interested.

Information just received from the office of Dr. Charles L. Parsons shows that there will be no meeting this spring of the Fertilizer Division and the newly organized Leather Section.



HARRY A. CARPENTER
Information



J. ERNEST WOODLAND
Executive

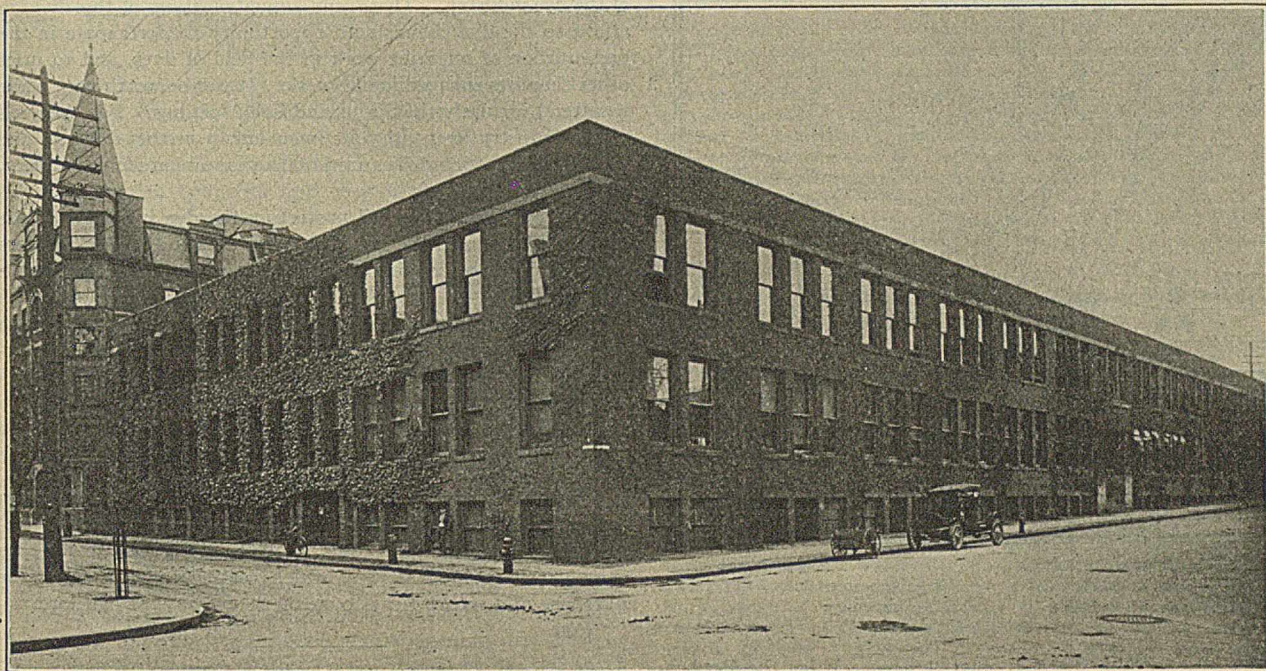


ERLE M. BILLINGS
Program



HARRY LEB. GRAY
Hotels

LOCAL COMMITTEE CHAIRMEN



MECHANICS INSTITUTE

The large general meeting will be held at the Chamber of Commerce, 67 St. Paul St., on Tuesday, April 26. The addresses of welcome will be delivered by Hiram Edgerton and by V. Roy McCanne, president of the Rochester Chamber of Commerce. Dr. Smith will respond, as president of the SOCIETY. Representative Nicholas Longworth, author of the Longworth Bill, and Senator James W. Wadsworth, Jr., the staunch friend of the Chemical Warfare Service, will be among the speakers. The general meeting will be continued in the afternoon at Convention Hall, Clinton Avenue, South. The evening is to be given to various college and fraternity dinners.

The large public meeting, to which the citizens of Rochester are especially invited, is to be held on the evening of Wednesday, April 27, at Convention Hall, and not at the Central Church, as originally announced. Dr. Charles F. Chandler has accepted the invitation to make the address at this meeting. The Good Fellowship Meeting will take place on the following evening in the dining hall at the plant of Bausch & Lomb. The program, in other respects, is practically as originally published.

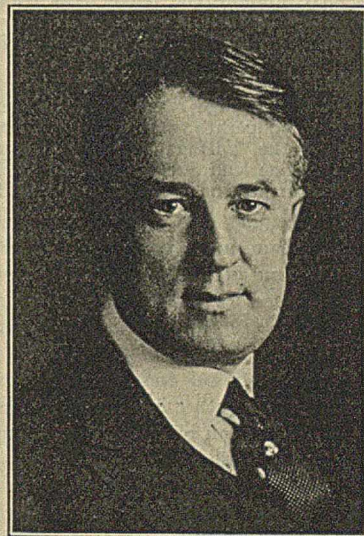
As Rochester is in so many ways a chemical center, the population is already deeply interested in the approaching meeting. The newspapers have for several weeks been printing in detail the news relating to the arrangements made by the local committees. Their interest has not only been fed but most skilfully stimulated by Mr. Benjamin V. Bush, the chairman of the Publicity Committee of the Rochester Section. There is no city in the country where more attention is bestowed upon the activities of the resident chemist than is given by the newspapers of the Flower City. The indications are, therefore, that the proceedings of the Spring Meeting will be fully and accurately reported.

There went up a cry from ancient Egypt, from a most ingenious people, that it could not make bricks without straw; and likewise it is difficult even for good reporters to make reports out of whole cloth. The work of reporting the proceedings at Rochester will be greatly facilitated if authors of papers which have a popular interest will send in abstracts of them to the A. C. S. News Service, One Madison Avenue, New York City, as far ahead of time as they can. These abstracts of four or five hundred words each are made into the form of bulletins, which are issued to the

news associations of the country as near ten days in advance of the delivery of the papers as possible, subject to the usual form of newspaper release. The principal factor in getting the work of the Spring Meeting to the attention of the American press is in the clearly written popular abstract prepared in time to make its distribution nationwide. Such material should be in as nontechnical language as is consistent with precision.

The Press Room this spring will be in the Mechanics Institute, where unusual facilities for serving the members of the Fourth Estate will be provided.

As THIS JOURNAL goes to press, the members of the local committee are making every endeavor to see that the hotel accommodations are adequate and that everything will be in readiness to give the welcome of an overflowing hospitality to the members of the largest scientific body in the world.

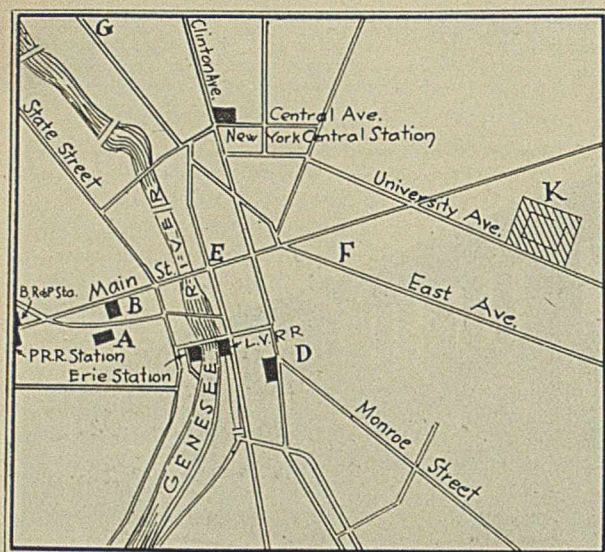


FRANK W. LOVEJOY
HONORARY CHAIRMAN, CONVENTION EXECUTIVE
COMMITTEE

.....

INITIAL MEETING OF THE PETROLEUM SECTION

The organization of a Petroleum Section has been authorized by the officers of the AMERICAN CHEMICAL SOCIETY, and it is proposed to hold the initial meeting of this section at the general meeting at Rochester. Dr. Thomas G. Delbridge, of the Atlantic Refining Company, Philadelphia, Pa., has been appointed chairman, and Dr. W. A. Gruse, of Mellon Institute,



- A—Mechanics Institute
B—Hotel Rochester
D—Convention Hall
E—Chamber of Commerce
F—Rochester Club
K—University
G—Bausch & Lomb

Pittsburgh, Pa., has been appointed secretary for the Rochester meeting.

The purpose which this organization is expected to fulfil may be expressed as follows:

(1) To enable chemists and technologists engaged in the petroleum, shale-oil, and natural gas industries to meet and to correspond, and to accumulate trustworthy information regarding the geochemistry of petroleum, oil-shale, and natural gas, the conversion of the raw materials into manufactured products, and the characteristics and usages of these products, together with their transport and storage.

(2) To promote the better education of persons desirous of becoming petroleum engineers, refinery engineers, or hydrocarbon chemists, and to elevate the professional status of those employed in the industries mentioned by establishing a high standard of scientific and practical proficiency.

(3) To encourage research in hydrocarbon chemistry.

(4) To coöperate with the American Petroleum Institute and with the National Research Council, and to collaborate with the American Society for Testing Materials in its work on the standardization of bituminous and petroleum products.

Fifty chemists and chemical engineers actively engaged in the petroleum industry have pledged their support and coöperation, and fifteen papers on the chemistry of petroleum have been promised for the first meeting. At this meeting it is desired also to take up such questions as that of the degree and scope of the activities of the section, the form of coöperation with other technical and scientific societies, the exact name of the section, and other interesting points. If time permits, it is planned to hold an informal symposium on the problems of the petroleum and allied industries.

All members of the SOCIETY who are interested, and all other persons who desire to become members of the section, are requested to send their names to its secretary, W. A. Gruse, Mellon Institute, Pittsburgh, Pa. A full attendance at this organization meeting is urged and the submission of papers is solicited.

The secretary will be glad to have any suggestions which this announcement may call forth.

TO THE DYE CHEMISTS

On Wednesday and Thursday, April 26 and 27, the Dye Division will assemble as a part of the 1921 Spring Meeting of the SOCIETY.

Scientific work is, has been, and always will be the backbone

of the dye industry. These semi-annual meetings of the division afford to the dye chemists an opportunity to participate in the presentation of scientific work in the field of dyes, and to meet other chemists engaged in like work. It will be worth your while to attend regularly the Spring and Fall Meetings. For the good of the industry keep up your membership in the division and induce others to join (dues are \$1.00 a year and are for stationery, postage, and the like).

The Longworth Dye Bill protecting the dye industry will be introduced again in the new Congress. Write to your Senators and to your Representative in Congress, urging an early passage of this bill.

Finally, plan to attend the Rochester meeting and endeavor to present a paper before the division. Send title to the secretary, R. Norris Shreve, 43 Fifth Ave., New York City.

SPECIAL RAILROAD RATES

A special one and a half fare on the certificate plan has been granted, if 350, carrying certificates, attend the meeting. Members must pay full fare going, taking certificates at the time they purchase their tickets, which certificates will allow the purchase of a return ticket over the same route at half fare.

Philadelphia College of Pharmacy Celebrates One Hundredth Anniversary

The one hundredth anniversary of the beginning of pharmaceutical education in America was celebrated in Carpenter's Hall and the Auditorium of the Philadelphia College of Pharmacy on the afternoon and evening of February 23, 1921.

The Philadelphia College of Pharmacy and Science is the outgrowth of the Philadelphia College of Apothecaries organized in historic Carpenter's Hall, Philadelphia, by the pharmacists of that city on February 23, 1821. Before that date there had been no organized courses in pharmacy for the training of druggists at any of the universities or colleges then in existence. The pharmacists of that period, recognizing the need for education in their profession, united to organize the Philadelphia College of Apothecaries, which later became the Philadelphia College of Pharmacy and has recently become, through charter amendment, the Philadelphia College of Pharmacy and Science.

The Founders' Day Celebration of the College took the form of a short meeting at Carpenter's Hall on the afternoon of February 23 in which the descendants of the founders of the College, the present officers, faculty, and members of the college took part. When they had assembled in the same room where the founders of the college met, Dr. C. A. Weideman, the present secretary of the College, read the minutes of the first three meetings of the founders. Mr. George M. Beringer, the chairman of the Board of Trustees, then gave a brief resumé of the progress that has been made by the institution in the past one hundred years. The ceremony was very impressive and was followed in the evening by a larger meeting in the auditorium of the College. Over six hundred officers, faculty, alumni, students, and friends of the College gathered at the evening meeting and listened to impressive addresses by Mayor J. Hampton Moore of the City of Philadelphia, Dean Charles H. LaWall of the Philadelphia College of Pharmacy and Science, Professor H. V. Army of the College of Pharmacy of Columbia University, and Dr. S. P. Sadtler, Emeritus Professor of Chemistry of the Philadelphia College of Pharmacy and Science.

The College is planning an endowment and building fund campaign for the purpose of enlarging the educational facilities which have been sorely taxed in the past few years.

New York Chemists' Club Confers Honorary Membership

The tenth anniversary of the opening of the present club house of the Chemists' Club, New York, was fittingly celebrated on the evening of March 17, 1921, by the award of honorary membership in the Club to eight distinguished chemists, four from foreign countries and four Americans, and by the presentation of the results of two splendid researches by Dr. Jacques Loeb and Dr. Irving Langmuir, respectively.

The fact that the Chemists' Club of New York is a national institution and in some respects international in scope was never more forcibly brought out than at this celebration. The presence of representatives of the embassies of Belgium, France, Great Britain, and Italy, who represented the scientists of the respective countries upon whom honorary membership was conferred, and the gathering of nonresident members from various sections of the country with those who reside in the Metropolitan District, bore testimony to the unique position which this Club has attained in scientific and social circles.

Early in the evening an informal reception to those selected for honorary membership and their representatives was held in the social room of the Club. This was followed by a dinner in their honor, after which adjournment was taken to Rumford Hall, where the principal exercises of the evening were held.

In a few well-chosen words Ellwood Hendrick, president of the Chemists' Club, stated the purpose of the gathering and introduced Dr. Charles Baskerville, chairman of the Committee of Arrangements, who gave a brief history of the organization and progress of the Club. Starting with eighty-nine men in 1898, the Club has grown to a total membership of 1728, a majority being nonresident members. Dr. C. F. Chandler, the first president of the Club, now in his eighty-second year, was present and was given an ovation when he was asked to rise. Dr. Baskerville referred feelingly to the untiring efforts of the late Morris Loeb, who contributed so much in energy, time, and money to the launching of the present club house, which was first occupied ten years ago.

Dr. Baskerville called attention to the fact that according to the constitution and by-laws of the Chemists' Club, honorary membership is limited to ten foreign and ten American scientists and election is by the unanimous vote of the trustees. He then announced that the following distinguished chemists would have honorary membership conferred upon them: Professor Giacomo Ciamician, University of Bologna; Professor H. L. LeChatelier, Collège de France; Dr. Ernest Solvay, Brussels; Sir Edward Thorpe, Imperial College of Science and Technology; Dr. John Uri Lloyd, Past President, American Pharmaceutical Association; Dr. W. H. Nichols, Past President of the American Chemical Society and Society of Chemical Industry; Dr. Edgar Fahs Smith, Past and Present President, American Chemical Society; and Dr. Edward Weston, the eminent physical chemist.

PROMINENT CHEMISTS PRESENT HONORARY MEMBERS

Dr. Bernhard Hesse presented Dr. Ernest Solvay—represented by Consul General Mali, of Belgium—as follows:

Founder of the ammonia-soda process, for three score years a pioneer and leader in industrial chemistry, whose activities have enormously developed the production and use of sodium products over all the world, and likewise have profoundly stimulated dependent and related industries; a leader in the application of scientific study to industrial problems; founder and indefatigable supporter of many institutions devoted to science, to public health and welfare, and to the elevation of human intercourse and relations; a source of great strength to his country in her peril, and a shining mark for the vengeance of her despoilers. The members of The Chemists' Club proclaim their admiration and esteem by election to Honorary Membership.

Professor Marston T. Bogert presented Professor Henri L. LeChatelier—represented by Consul General Liebert—as follows:

Professor at Collège de France and at l'École des Mines, member of the Académie des Sciences, for over forty-six years an active, resourceful, fruitful, daring and original investigator of the fundamental principles underlying chemical action and thermodynamics. He has enriched our knowledge with countless facts and with many sound and far-reaching theories based upon them; and he has greatly influenced and enhanced the arts of metallurgy, of electrometallurgy, and of applied chemistry generally. He was called on by his country in her time of stress to bring his profound knowledge and experience to bear upon the solution of problems vital to her preservation and necessary to her progress, and on the return of peace he was honored by her with many prizes and medals. To him the members of The Chemists' Club tender evidence of their profound esteem by election to Honorary Membership.

Dr. Landis presented Sir Edward Thorpe—represented by Counsellor Broderick of the British Embassy—as follows:

Born near Manchester, a student of science at Owens College, the Universities of Heidelberg and Bonn, a brilliant teacher in several colleges in his native land, at the age of three-quarters of a century he is Professor of Chemistry Emeritus of the Imperial College of Science and Technology, South Kensington. For many years director of the Government Laboratories in London, his accuracy of methods of analysis and clarity in their exposition, coupled with a wisdom as to human purposes in the interpretation of law, gave a model for municipal experts in caring for the welfare of his fellow citizens. His delightful biographies of famous chemists are examples of charming literary style for others to study and follow. His Dictionary of Applied Chemistry is an authoritative work, turned to by all seeking full knowledge. His researches in pure chemistry carried him to the presidency of the Chemical Society of London; his exposition and knowledge of technology were recognized a generation ago by a similar demand on the part of the Society of Chemical Industry; and his breadth of appreciation of all science likewise brought him the vice presidency of the British Association for the Advancement of Science and the Royal Society. His eminence as a scientist, technologist, and author, commanding several languages, for he had a large personal acquaintance with savants of foreign tongues, burdened him with Honorary and Corresponding Memberships in numerous scientific, literary, and philosophical academies and societies of other lands. Many times doctored, this Fellow of the Royal Society will long remain a teacher of power, even to many who may never hear his voice. We honor ourselves in electing him to be one of that limited number to whom The Chemists' Club can pay such tribute.

Professor Maximilian Toch presented Professor Giacomo Ciamician—represented by the Italian Ambassador, Rolando Ricci—as follows:

Senatore del Regno, professor of general chemistry at the University of Bologna, for more than forty-two years an active, ingenious, fruitful, and original investigator in pure organic chemistry, applying it to determine the nature and mechanism of the origin of constituents of plants and animals, and the influence therein of sunlight, uncovering many facts which have finally enabled him so to correlate these phenomena that our view of them has become greatly clarified, and much firm ground for further and beneficial advance in this most intricate field has been created. The members of The Chemists' Club elect him to Honorary Membership in recognition of his eminence in science and in appreciation of an associated ally in a holy cause.

Dr. Bloede presented Dr. John Uri Lloyd—represented by Dr. Alfred Springer, of Cincinnati, Dr. Lloyd being ill—as follows:

Born in New York State, a student of nature and of people, trained in a severe school of experience in Kentucky, he rose to the professorship of chemistry in the Cincinnati College of Pharmacy and to the presidency of the American Pharmaceutical Association. By his investigation in phytochemistry, especially applied to medicine, he created new knowledge of alkaloids, glucosides, and the physiological variations in reactions of drugs, especially as colloids. A graceful and imaginative pen has augmented his contributions to scientific literature and perpetuated his close and accurate study of the dialect, superstition, and folklore of the Blue Grass Country. His "String Town" alone has aroused interest in chemistry and given pleasure to over a million people. He, with his brother, has handsomely housed one of the most complete libraries of botany and chemistry in the world, permanently endowed it, and given it *in perpetuo* to the city wherein he struggled as a youth, conquered as a strong man, and now lives, surrounded by affection and esteem. Over three score years and ten find him still active in the laboratory and in public affairs. Numerous honors have come to him and are deservedly his. To them the members of The Chemists' Club take this, their best means, of adding appreciation of his diligent and fruitful labors for human welfare and happiness.

Professor Wilder D. Bancroft presented Dr. W. H. Nichols in person, as follows:

For more than fifty years successfully engaged in those branches of industrial chemistry of fundamental importance to the development of

our country, at many places and in every section of this continent; a firm believer in the application of science to industry and always its consistent follower in practice; a staunch and helpful leader and supporter in securely expanding the study of chemical science, research, and application in all branches of our educational system; far-sighted in the promotion of international understanding among chemical associations and chemists, and for many years with rare patience and discernment creating and fostering opportunities for scientific, technical, and social cooperation among the chemists of the United States to the permanent benefit of all. His constructive capacity carried him to the presidency of the American Chemical Society, of which he was one of the founders. His world-wide recognition brought the presidencies of the Society of Chemical Industry and Eighth International Congress of Applied Chemistry. Among the numerous honors and distinctions which have come to him, we, the members of The Chemists' Club, desire to include our appreciation of his great services on behalf of Science, Business, and the Welfare of Mankind, by electing him to Honorary Membership.

Dr. Charles Reese presented Dr. Edgar F. Smith in person, as follows:

Again president of the American Chemical Society after a lapse of twenty-five years; one to whom that Society owes much for devoted and self-forgetful service in its pioneer days; connected with the University of Pennsylvania as educator and administrator for over forty years; a scientist whose researches have covered widely separated fields in electrochemistry, the rare earths, and atomic weights; author of standard texts on electrochemistry, as well as translator of foreign texts; a historian who adds to a charming literary style the painstaking accuracy and attention to detail which have made him a brilliant teacher and scientist. To the innumerable evidences of esteem and affection on the part of students, colleagues, and citizens, we, the members of The Chemists' Club, desire to add ours by his election to Honorary Membership.

Dr. Cottrell presented Dr. Edward Weston in person, as follows:

Of English birth, for over fifty years an American chemist, physicist, and inventor; a scientific investigator of absolute integrity, he has brought to the solution of physical and electrical problems the chemist's point of view. He has been an early worker in the electroplating field, he perfected the dynamo for use in that art; was inventor of the recently rediscovered flaming arc; was one of the pioneers in the development of the incandescent lamp and filament. He is the inventor of standard electrical measuring apparatus. This work involved detailed and long-continued researches on alloys, and the results have led to entirely new views on the nature of metals and non-metals. A wise counselor in the affairs of The Chemists' Club, the members elect this friend and scientist to Honorary Membership as an evidence of affection and esteem.

Each recipient of the certificate of honorary membership was roundly applauded in turn, and the newly created honorary members or their representatives took seats on the stage under the flags of their respective nations. It was a ceremony which should link to an even greater degree the chemists of the allied countries with their brother chemists in America.

DR. LOEB DISCUSSES RESEARCH ON PROTEINS

The second part of the program was devoted to the presentation of two highly interesting and perhaps epoch-making investigations. Dr. Jacques Loeb, of the Rockefeller Institute, presented an account of his researches on "The Chemical and Physical Behavior of Protein Solutions." Dr. Loeb stated that life is so closely linked to the chemical and physical properties of proteins that the knowledge of their properties must precede the attempt to unravel the dynamics of living matter.

The modern concepts of colloid chemistry have been used to supply this knowledge, and foremost among these is the idea that the reactions of colloids in general and proteins in particular are not determined by the purely chemical forces of primary valency, but by the rules of adsorption; and that the influence of electrolytes on the physical properties of proteins is due to an alteration in the degree of dispersion or in the degree of hydration of the protein particles. From his experiments Dr. Loeb has reached the conclusion that the views summarized above are based on a methodical error as far as the proteins are concerned; namely, on the failure to take into consideration the hydrogen-ion concentration which happens to be the chief variable in the chemistry and physical chemistry of proteins. When this variable is duly considered, it is

found that the laws of classical chemistry account for the chemical and at least a part of the physical behavior of the proteins. Dr. Loeb then gave an account of his experiments in detail. He showed that proteins combine by the purely chemical forces of primary valency and in strictly stoichiometrical proportions with acids and alkalies. Experiments based on the measurement of the hydrogen-ion concentration have led Dr. Loeb to the conclusion that the physical properties of proteins, such as osmotic pressure, swelling, viscosity, and potential difference, are not affected by the nature of the ion in combination with the protein but only by the valency. This fact finds its explanation in the Donnan membrane equilibrium. Furthermore, Dr. Loeb has shown through his experiments that the influence of the hydrogen-ion concentration on the P. D. and on the osmotic pressure of protein solutions can also be accounted for not only qualitatively but quantitatively by Donnan's theory. Dr. Loeb stated that Procter's experiments and some of his own experiments which are not yet complete suggest that the influence of the hydrogen-ion concentration and of the valency of the anion on the swelling of gelatin-acid salts may possibly be explained in the same way. The classical laws of general and physical chemistry therefore furnish us with a quantitative theory not only of the chemical behavior of proteins, but also of at least some of their physical properties.

DR. LANGMUIR PRESENTS THEORIES ON DEDUCTIVE CHEMISTRY

Dr. Loeb's address was received with great applause, and President Hendrick then introduced Dr. Irving Langmuir, of the Research Laboratory of the General Electric Company, who spoke on the "Influence of Physics on Modern Chemical Thought." Dr. Langmuir believed that the work of the physicist will have an increasing influence on the development of chemistry in the coming years. He referred to the new aspect in chemical viewpoints that has developed in the past decade, and particularly to the new theories regarding the constitution of the atom. He believes that when once the constitution of the atom is definitely known, chemistry will become a deductive science. We would not have to rely on experiments to determine the properties of chemical compounds, for they could be accurately deduced. The speaker reviewed some of the theories which had been advanced regarding the condition of the electrons in the atom and pointed to the dominating influence which atomic structure is beginning to exercise because of the clear understanding it will give of chemical relationships. At the present time, said Dr. Langmuir, the chemist bases his predictions on a certain intuition which comes with long experimental practice, and also on mature judgment resulting from laboratory experiences. Once the structure of the atom is solved, more dependable methods will be available to the chemist for deducing the properties of compounds and probable reactions. Dr. Langmuir then pointed to the fact that Coulomb's law supplementing the theory of valence almost eliminates what he calls chemical intuition as to which compounds are stable and which are unstable. By the same means it is possible to calculate energy values, and Dr. Langmuir believes that with a little more experimenting he will be able to calculate the heats of reaction of various chemical substances.

It is very necessary for the development of chemistry, in Dr. Langmuir's opinion, that the student should learn the new views based on the development of the past one hundred years, rather than crowd his mind with a study of the beginnings of chemistry and the many progressive steps that have been necessary to arrive at the present state of our knowledge of the subject. He believes that once atomic structure is solved, 90 per cent of the study of chemistry will be deductive. Dr. Langmuir felt that the goal to which we should look forward is the prediction of chemical properties and relationships without the necessity of going through a long series of experiments.

More and quicker progress can be made by deduction than by experimentation. The fundamental thing to be determined is whether the electrons in the atoms are moving or whether they are stationary, as this will give us the key to atomic structure. If they are moving in orbits, the task will be very difficult; if they are stationary, the task will be comparatively easy.

The applause which followed Dr. Langmuir's presentation showed that those present realized that chemistry is on the threshold of a rapid development, and that they had possibly listened to the beginning of a new epoch of progress in the fundamental principles underlying the entire structure of this science.

Colloid Development

The Committee on the Chemistry of Colloids, appointed by the National Research Council, feels that interest in colloid chemistry is growing rapidly. No better evidence of this could be found than the Symposium on Colloid Chemistry at the Society's meeting in St. Louis, in April 1920. The other divisions all adjourned in favor of the symposium, and eight hundred chemists crowded into the room. Probably two hundred stood for an hour or two. Comments on the program showed very great interest by the audience.

In THIS JOURNAL, XI (1919), 794, we offered a number of lectures by members of the committee and others. There was a ready response. Within a year about one hundred such lectures were given before universities and sections of the Society. New England, the South, the Middle West, California, and the Northwest availed themselves of the offer. This method of stimulating interest paid. More of these lectures are being given this year at various institutions.

In response to the request of the committee, W. D. Bancroft has written and published a stimulating book on "Applied Colloid Chemistry." We need more courses in the subject, and proper texts and laboratory manuals help to make this possible. For the same reason the chairman has nearly completed a "Laboratory Manual of Colloid Chemistry," to be published in the near future. A classified bibliography with brief comment is also being prepared. This will probably be issued in a very incomplete condition in mimeograph form. Copies will be distributed for criticism and suggested additions. The final product will then be published in some suitable manner. In the meantime, chemists can render valuable assistance by sending the chairman references to their favorite colloid fields. The comment need not exceed fifty words. This is not to be an abstract of each article but a sign post to show the reader whether or not it is worth his interest.

The list of "Research Problems in Colloid Chemistry," now being published in THIS JOURNAL by W. D. Bancroft, is another part of our plan. No sooner had the first instalment appeared than the chairman received decidedly interesting letters of inquiry.

The suggestion that the committee be made a sort of clearing house for the colloid chemists and the manufacturers brought out a ready response. Requests have come in for highly trained colloid chemists, but as yet such men are few in number. More must be trained at once. Two very great dye companies have asked for help. A manufacturer in another line recently offered to pay as high as \$7500 for the right colloid chemist. Evidently no missionary work was needed to convince this man of the importance of colloid chemistry in the industries. Unfortunately, the vigorous development of our subject in this country is too recent to have created an adequate supply of the men needed.

The chairman suggested to one manufacturer asking for help that the company select a young man equipped with his Ph.D., and possibly some experience, and send him to any one of three or four institutions that might be named, for a year's training in colloid routine and research. This should be on salary, of course. The manufacturer, by this method, selects a man

for his fundamental training and personality and adds to this the specialization desired. The teacher in charge of the young man gains in having a trained research assistant. Industrial men must face the situation squarely. If they want highly trained colloid chemists they must help in their training.

One of our leading physical chemists urges that we publish from time to time, revised lists of books on colloid chemistry. Such a list follows:

BRIEF BIBLIOGRAPHY

- 1—Emil Hatschek: "An Introduction to the Physics and Chemistry of Colloids," 116 pp. P. Blakiston's Son & Co., Philadelphia, 1919. Based on a course of ten lectures. A remarkably clear introduction to colloids. Third edition. A laboratory manual has since been written by Hatschek.
- 2—Jerome Alexander: "Colloid Chemistry," 90 pp. D. Van Nostrand Co., New York City, 1919. Deals largely with the practical applications of the science.
- 3—Bayliss: "Principles of General Physiology." Longmans, Green & Co., New York City, 1915. In pp. 74-110 is given a clearly written introduction to the "Colloidal State."
- 4—Wolfgang Ostwald: "Theoretical and Applied Colloid Chemistry." Translated by Martin Fischer. 232 pp. John Wiley & Sons, Inc., New York City, 1917. Revision of a course of five lectures given in the United States a few years ago. A very stimulating book.
- 5—W. D. Bancroft: "Applied Colloid Chemistry." 343 pp. McGraw-Hill Book Co., Inc., 1921. Written at the request of the Committee on the Chemistry of Colloids. A delightful book, full of illuminating comments on the work recorded in the literature. Especially strong in treatment of adsorption. Every colloid chemist should own this book.
- 6—Zsigmondy: "The Chemistry of Colloids." Translated by Spear. 288 pp. John Wiley & Sons, Inc., New York City, 1917. Probably the most useful book of its size on the subject yet published. Contains 33 pages on the industrial applications of colloids.
- 7—Freundlich: "Kapillarchemie." 591 pp. Leipzig, 1909. The greatest classic in the literature of colloids.
- 8—Wolfgang Ostwald: "Handbook of Colloid Chemistry." Translated by Martin Fischer. 278 pp. P. Blakiston's Son & Co., Philadelphia, 1915. Gives valuable references to the literature. A translation of Ostwald's "Grundriss der Kolloidchemie."
- 9—Bechold: "Colloids in Biology and Medicine." Translated by Bullowa from second German edition. 464 pp. D. Van Nostrand Co., New York City, 1919. A splendid book; somewhat specialized as the title indicates, but valuable to any student of colloids. Contains 40 pages on "Methods of Colloidal Research," including much of the author's own work on ultrafiltration.
- 10—Taylor: "Colloids." 327 pp. Longmans, Green & Co., New York City. Not well arranged. Contains some useful directions for the preparation of colloids. Should be used only as a reference book on isolated points.
- 11—Burton: "Physical Properties of Colloid Solutions." 197 pp. Longmans, Green & Co., New York City, 1916. Contains a useful bibliography. Rather physical in treatment.
- 12—The Svedberg: "Herstellung Kolloider Lösungen." 507 pp. Theodor Steinkoff, Dresden, 1909. A classic. Gives full directions for preparing hundreds of colloids. Contains a valuable bibliography.
- 13—Martin Fischer: "Oedema and Nephritis." 2nd Ed. 695 pp. John Wiley & Sons, Inc., New York City, 1914. Outlines and defends a treatment of disease based on the principles of colloid chemistry.
- 14—First, Second and Third Reports on Colloid Chemistry and Its General and Industrial Applications, by the British Association for the Advancement of Science. At H. M. Stationery Office, 128 Abingdon St., London, S. W. 7. Each report (about 160 pp.) contains chapters on special fields by eminent authorities. Thorough reviews, numerous references. An invaluable colloid library. Each report costs 2/6 d.
- 15—A Laboratory Manual of Colloid Chemistry written by Harry N. Holmes at the request of the Committee on Colloids will be published in the near future by John Wiley & Sons, Inc.
- 16—Martin Fischer and Marian Hooker: "Fats and Fatty Degeneration." 146 pp. John Wiley & Sons, Inc., New York City, 1917. Theories of emulsification discussed, especially in relation to body tissues.
- 17—U. S. Bureau of Soils, Bulletin 52; "Absorption by Soils." 95 pp. 1908. Very useful.
- 18—U. S. Bureau of Soils, Bulletin 51; "Absorption of Vapors and Gases by Soils." 1908.
- 19—Ashley: "Technical Control of the Colloidal Matter of Clays." U. S. Bureau of Standards, Technologic Paper 23. 115 pp. Written in 1911.
- 20—Bancroft: "Applied Colloid Chemistry." Chem. Met. Eng., 23 (1920), 451. A brief survey of the field.
- 21—W. C. McC. Lewis: "Some Technical Applications of Capillary and Electrocapillary Chemistry," Met. Chem. Eng., 15 (1916), 253-259; also J. Soc. Chem. Ind., May 31, 1916. Somewhat like the book by Alexander (No. 2).

22—Whitney and Ober: *J. Am. Chem. Soc.*, **23** (1901), 856-863. Gives an excellent bibliography, with brief comment, of colloid work published before 1901. Nearly 150 references.

23—A. Müller: "Bibliography of Colloid Chemistry," *Z. anorg. Chem.*, **39** (1904), 121. 356 references grouped by subjects, without comment.

24—Höber: "Physikalische Chemie der Zelle und Gewebe." Wilhelm Engelmann, Leipzig, 1911.

25—Rideal and Taylor: "Catalysis in Theory and Practice." The Macmillan Co., New York, 1919. Not primarily a colloid book but contains material of value to colloid chemists. A new edition is promised.

Kolloid-Zeitschrift and its *Beihfte* have devoted their columns exclusively to colloid research. Very important.

The *Journal of Physical Chemistry* contains a vast amount of invaluable material and no student of colloid chemistry can afford to neglect this journal. Many of the articles contain exceptionally full summaries of the work done in special fields, and are really monographs. The results of colloid research, however, are found in most of the great journals.

Since many chemists waste time and become discouraged by reading the wrong book first, we urge any one of the first three in the above list as the proper introduction to the subject.

OBERLIN, OHIO
OBERLIN COLLEGE

HARRY N. HOLMES, *Chairman*,
Committee on Chemistry of Colloids

Calendar of Meetings

Technical Association of the Pulp and Paper Industry—Spring Meeting, Waldorf-Astoria and Hotel Astor, New York, N. Y., April 11 to 14, 1921.

American Paper and Pulp Association—Annual Meeting, Waldorf-Astoria and Hotel Astor, New York, N. Y., April 11 to 15, 1921.

American Electrochemical Society—Spring Meeting, Hotel Chalfonte, Atlantic City, N. J., April 21 to 23, 1921.

American Chemical Society—Sixty-first Meeting, Rochester, N. Y., April 26 to 29, 1921.

American Oil Chemists' Society—Twelfth Annual Meeting, Chicago, Ill., May 16 to 17, 1921.

American Institute of Chemical Engineers—Spring Meeting, Detroit, Mich., June 20 to 21, 1921.

Seventh National Exposition of Chemical Industries—Eighth Coast Artillery Armory, New York, N. Y., September 12 to 17, 1921.

NOTES AND CORRESPONDENCE

Note on the Use of Potassium Permanganate in the Determination of Nitrogen by the Kjeldahl Method

Editor of the Journal of Industrial and Engineering Chemistry:

It was for a long time the practice in this laboratory to add potassium permanganate at the end of digestion in the determination of nitrogen. About a year ago it was decided to determine whether the addition of the permanganate was necessary. After making determinations for several weeks in which permanganate was added to one of the duplicates, we concluded that it had no effect and its use was discontinued. On that account we were surprised at the results obtained by Cochrane [*THIS JOURNAL*, **12** (1920), 1195]. The results of further experiments lead to the conclusion that the addition of permanganate is not necessary when sodium or potassium sulfate and mercury are used with the sulfuric acid in the digestion.

It was noted that Cochrane did not use either potassium or sodium sulfate and it seemed possible that the more uniform results obtained when he used potassium permanganate were due to the fact that the digestions were not complete at the end of 2.5 hrs. Several digestions were, therefore, made with sodium sulfate in one duplicate and none in the other. The results showed that the digestion is not complete within 2.5 hrs. if the sulfate is not added.

Our results are summarized in the following table:

SUBSTANCE	No. of Deter- minations	Per cent of Nitrogen			
		1	2	3	4
		KMnO ₄ Added Average	KMnO ₄ Added Average	Na ₂ SO ₄ and KMnO ₄ Added Average	Na ₂ SO ₄ and no KMnO ₄ Added Average
Cottonseed Meal A.....	2	6.993	6.822	7.043	7.043
Cottonseed Meal B.....	2	6.977	6.789	7.044	7.043
Wheat Mixed Feed A.....	2	2.720	2.712	2.784	2.730
Wheat Mixed Feed & Sc. A	2	2.470	2.444	1.488	2.461
Comp. Feeces A.....	2	1.342	1.394	1.344	1.400
Comp. Feeces B.....	2	1.360	1.283	1.360	1.400
Broom Corn Silage Refuse A	2	0.472	0.492	0.459	0.499
Broom Corn Silage Refuse B	2	0.464	0.486	0.424	0.483

C. T. DOWELL AND W. G. FRIEDEMANN

OKLAHOMA AGRICULTURAL EXPERIMENT STATION
STILLWATER, OKLAHOMA
January 20, 1921

Editor of the Journal of Industrial and Engineering Chemistry:

I would call attention to the fact that in five out of the eight

samples analyzed, the data presented in Columns 1 and 2 of the table support the conclusions drawn in my article.

No comparison was made in my article between the straight Kjeldahl method and the Gunning modification, nor were any data presented bearing on the use or non-use of permanganate in any method where sodium or potassium sulfate is used to raise the boiling point of the digestate.

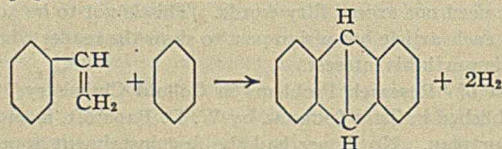
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.
February 5, 1921

D. C. COCHRANE

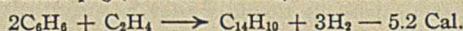
The Formation of Anthracene from Ethylene and Benzene—Correction

In our paper on the above subject [*THIS JOURNAL*, **13** (1921), 208] several self-evident errors escaped proof reading, and we wish to have them corrected though they do not in any way affect our results or conclusions.

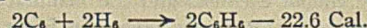
On page 208, first column, the reaction should read:



On the same page, second column, the reaction should read:



On the same page, second column, footnote, the change should be



and $\text{C}_{14}\text{H}_{10}$ instead of $\text{C}_{10}\text{H}_{14}$.

J. E. ZANETTI AND M. KANDEL

COLUMBIA UNIVERSITY
NEW YORK, N. Y.

The Estimation of Cellulose in Wood

Editor of the Journal of Industrial and Engineering Chemistry:

With the exception of a few attempts to determine the cellulose content of lignified materials by dissolving and reprecipitating the cellulose, it has been the object of all quantitative cellulose determinations to isolate the cellulose by dissolving out the noncellulose compounds. A complete removal of these compounds from a highly lignified substance, such as wood, without

attacking the cellulose proper has never been accomplished. But it is possible by careful manipulation to remove completely some of the noncellulose substances, such as rosin, lignin, and lower carbohydrates, from finely disintegrated wood; and to obtain a residue which does not contain decomposition products of the cellulose originally present as such in the wood. This residue, however, differs chemically from normal cellulose as represented by purified cotton, in that it yields an appreciable quantity of furfural on distillation with hydrochloric acid, probably owing to the presence of highly resistant pentosans.

Of the many methods that have been suggested for the quantitative determination of cellulose in wood, none have been more widely accepted than Cross and Bevan's¹ method, which is based upon the removal of the lignin by chlorination. The method was originally applied to jute fiber and included boiling of the fiber for one-half hour in a 1 per cent sodium hydroxide solution, treatment with chlorine gas for 30 to 60 min., and dissolving of the lignin chloride in a 2 per cent solution of sodium sulfite at boiling temperature. After washing, the fibers were finally bleached with potassium permanganate.

In applying the method to wood fibers, several investigators found that it was not possible to remove the lignin completely with one single chlorination, but that if the fibers were subjected to alternating treatments with chlorine gas and sodium sulfite, a complete removal of the lignin compound could be effected. Renker² obtained from wood a residue which did not give any of the lignin reactions, by repeating the treatment six times with a total time of exposure to the gas of 2.75 hrs. He also modified the original method by omitting the treatment with sodium hydroxide previous to chlorination, stating that he thereby obtained a considerably higher cellulose value with equal purity of residue. It is of importance for the following discussion to point out at this place that Renker based this statement upon the fact that the residue did not give the qualitative lignin reactions, while he did not analyze the residue with regard to furfural yield.

According to Renker the time of exposure to the chlorine gas should be as short as possible, since the cellulose itself is attacked by prolonged exposure to the gas, and he was supported by Heuser and Sieber,³ who found that under the action of chlorine gas a layer of lignin chloride is rapidly formed on the surface of the fiber, preventing further penetration of the gas. It is therefore necessary to dissolve this layer before the chlorination is continued, and in doing so it is possible to remove the lignin completely without injury to the cellulose. Sieber and Walter⁴ found that four chlorinations with a total exposure to the gas of 1 hr. were sufficient for the complete removal of the lignin in wood. They also allowed the fibers to remain in the same Gooch crucible with a stationary calico pad throughout the entire process of purification, thereby eliminating mechanical losses, which might occur when using Renker's method. Their method of manipulation has been adopted by recent investigators with the exception of Schorger, who used practically the same method as Renker.

The chlorination method has the advantage above other methods of cellulose determination of being a well-studied reaction, simple in operation and quick, and giving a residue free from lignin and without decomposition products of the original cellulose. But it was severely criticized by König and Huhn⁵ on account of the high furfural yield of the residue. These investigators proved that the furfural-yielding substances could be practically completely removed from the wood fiber by hydrolysis, but their method of accomplishing this, as well as the method proposed by Tollens and Dmochowsky,⁶ both of which methods include a hydrolysis with inorganic acids and both of which yield

a product free from lignin and practically free from furfural-yielding substances, cannot be recommended for quantitative estimation of cellulose, because, as I have shown, the cellulose itself is attacked and partly dissolved in the process of purification. It is a fact that the furfural-yielding compounds of the wood are subject to hydrolysis, but it is equally true that even very dilute inorganic acids attack normal cellulose.

Apparently the cellulose is much more resistant towards the action of organic acids. In fact Schwalbe and Johnsen¹ found that cellulose heated with a mixture of glycerol and acetic acid at 135° C. for several hours did not show any sign of attack as indicated by reducing power, and a method of estimating the cellulose content of commercial wood pulps which included this treatment was developed by them. Later, Johnsen and Hovey² suggested a method of cellulose determination in wood consisting of a 4-hr. hydrolysis with glycerol and acetic acid at 135° C., with a subsequent chlorination according to Sieber and Walter, and found that by employing this method a residue of higher purity could be obtained from wood fibers.

The subject of cellulose determination was recently discussed by Dore,³ who arrived at the conclusion that "all processes involving preliminary hydrolysis result in a diminished yield of cellulose as well as total cellulose and are therefore unacceptable as accurate cellulose processes." Partly on the basis of this statement, partly on his own observations, Mahood⁴ in a more recent contribution to the subject states that "The modification of the Cross and Bevan method proposed by Johnsen and Hovey appears to be of doubtful value since the cellulose, as well as the hemicelluloses and furfural-yielding constituents, are attacked."

In view of the importance of the subject under discussion, it would seem advisable to prove such statements by convincing experimental data. But Dore, as well as Mahood, has failed to do so, and I hope to be able to show in this article that the conclusions arrived at by the two investigators are based upon insufficient analytical data and upon statements which are misleading and partly incorrect.

In order to facilitate the discussion of some of the experimental results, two tables taken from Dore's publication are copied below:

TABLE II—COMPARISON OF METHODS OF PRELIMINARY HYDROLYSIS AS APPLIED TO WOODS

Results in percentages of air-dry wood (11.62 per cent moisture)

	TOTAL CELLULOSE		α-CELLULOSE		Ratio α-Cellulose: Total Cellulose
	Individual	Average	Individual	Average	
(1) Renker's modification of Cross and Bevan's method. No hydrolysis	47.93 48.46 48.97 48.77 48.91 48.27 48.24	48.51	36.04 36.02 36.71 36.84 37.09 36.76 36.99	36.64	0.75
(2) Original Cross and Bevan method. 1 hr. with 1 per cent sodium hydroxide at boiling temperature	45.86 46.28 45.85 45.07 45.64 46.29	45.83	35.38 35.49 35.25 35.03 35.76 35.55	35.41	0.77
(3) Johnsen and Hovey method. 4 hrs. with acetic acid and glycerol at 135° C.	44.04 44.11 44.37 44.49		34.60 34.73 34.70 34.53	34.64	0.78

TABLE III—FURFURAL YIELD OF PRODUCTS
In percentages of air-dried material (11.62 per cent moisture)

	FROM TOTAL CELLULOSE		FROM α-CELLULOSE	
	Individual	Average	Individual	Average
(1) Renker's process. No hydrolysis	2.66 2.36 2.69 2.38	2.52	0.52 0.48 0.51	0.50
(2) Cross and Bevan's process. Alkaline hydrolysis	2.67 2.63	2.65	0.31 0.24	0.27
(3) Johnsen and Hovey's process. Acid hydrolysis	2.18 2.20	2.19	0.25 0.27	0.26

¹ "Cellulose," London, 1918, 94.

² "Bestimmungsmethoden der Cellulose," Berlin, 1910.

³ *Z. angew. Chem.*, **26** (1913), 801.

⁴ *Papier-Fabr.*, **11** (1913), 1179.

⁵ "Bestimmung der Cellulose in Holzarten und Gespinnstfasern," Berlin, 1912.

¹ *Pulp Paper Mag. Can.*, **13** (1915), 600.

² *J. Soc. Chem. Ind.*, **37** (1918), 132.

³ *THIS JOURNAL*, **12** (1920), 264.

⁴ *Ibid.*, **12** (1920), 873.

The determination of α -cellulose gives, of course, an excellent indication of the purity of the residues, provided the α -cellulose is a well-defined substance. Table II, however, shows that this is not so, since the furfural yield of the α -cellulose obtained from Renker's process is considerably higher than of that obtained with Johnsen and Hovey's method. The α -cellulose from the latter process yields 0.26 per cent furfural, which is very close to the yield from purest cotton cellulose,¹ *e. g.*, 0.24 per cent. With regard to furfural yield and α -cellulose content of the residues, it will also be seen from the two tables that the cellulose resulting from Johnsen and Hovey's method is of a higher purity than that from Renker's method (no hydrolysis), which latter accordingly must give a higher yield. Assuming that the furfural originates with highly resistant pentosans (which has never been disproved), the difference in yield of pentosan-free α -cellulose with the two processes was only 1.58 per cent, while the difference in total cellulose in the two processes was 4.26 per cent, which shows that Dore's statement that the total cellulose and the α -cellulose "are destroyed in the same proportion" is incorrect.

The difference of 1.58 per cent in the yield of α -cellulose does not necessarily mean that the normal cellulose is attacked in the hydrolytic treatment. The possibility naturally exists that a cellulose which has been exposed to acid hydrolysis is more easily attacked by strong alkali than a cellulose which has not received this treatment. But it is more probable that the difference in yield is caused by the removal of carbohydrates other than pentosans and less resistant than cellulose. Apparently Dore, as well as Mahood, is inclined to consider as cellulose all substances in the cellulose residue which do not give furfural reaction. This can hardly be accepted as correct since we must assume the presence of hexosans of less resistance than cellulose, and which therefore can be separated from the cellulose proper by hydrolysis, but by a more effective hydrolysis than that obtained with sodium sulfite at 100° C.

This would explain the considerably lower yield of cellulose in the commercial wood pulp processes than the yield indicated by the cellulose determination, since the commercial processes include hydrolysis at high temperature and pressure. It would also explain why the yield obtained with Johnsen and Hovey's method is lower than that of Renker's method, because the former includes an acid hydrolysis with acetic acid in glycerol at 135° C. Since this process removes the more resistant furfural-yielding substances and hexosans to a larger extent than Renker's method, the residue is more identical with the pulps obtainable in the commercial processes. Johnsen and Hovey therefore considered their method "very useful in the valuation of the various woods for the commercial paper pulp processes."

Dore concludes that "the hydrolytic processes do not remove any appreciable amount of the furfural-yielding complexes from the product." But there are no experimental data in Dore's article to prove this conclusion, while Johnsen and Hovey's publication shows that with their method over 10 per cent more of the total furfural-yielding substance is removed, or that between 22 and 25 per cent of these substances still remaining in the residue from Renker's method are removed with their method.

In discussing the removal of these substances by acetic acid hydrolysis, Mahood states that "approximately the same result could be attained by a further chlorination of the sample than usual." But this is not so, since apparently the furfural-yielding constituents, while being comparatively easily hydrolyzed, are very resistant to chlorination or oxidation. Furthermore, it must be remembered that it is not permissible in a quantitative method to continue the chlorination after the total lignin has been removed, since this would result in an oxidation of the cellulose proper.

Mahood's strong criticism of the Johnsen and Hovey method is based to a very great extent upon Dore's experiments, according

to which the normal cellulose is destroyed by hydrolysis with acetic acid in glycerol at 135° C. For these experiments Dore selected as normal cellulose "a piece of cotton sheeting which had been repeatedly laundered and might therefore be considered a residue consisting of highly resistant cellulose, mostly of the normal type." This is fundamentally incorrect, since it is well known that the resistance of cotton cellulose is considerably reduced by laundering. On the other hand, Schwalbe and Johnsen have found that the hydrolysis with acetic acid in glycerol does not attack the cellulose. Purest cotton cellulose hydrolyzed with this mixture and subsequently treated with nitrous gases lost only 0.12 per cent of its weight. Unfortunately this work has not yet been published in detail, but it has been referred to in recent publications by Johnsen¹ and by Schwalbe.¹

In conclusion, the writer wishes to refer to two statements in Mahood's article, because they are in disagreement with the results obtained by other investigators, and should therefore be more thoroughly investigated. Mahood found that there was an appreciable loss in weight of the fibrous filter pad used in the Gooch crucible, owing to the action of chlorine. When using unpurified calico Sieber and Walter recorded a loss of 0.001 g. A purified calico pad gained 0.0002 g. in the treatment. Sieber and Walter also found that cooling did not have any influence upon the yield, while Mahood believes that the lower yield of cellulose which he experiences with Sieber and Walter's modification of the method as compared with the original method is due to the higher temperature.

Sieber and Walter's modification of Renker's method represents a decided improvement in the process in mechanical manipulation, in that it eliminates mechanical losses of fiber, and the method has therefore been adopted by most of the recent investigators and by commercial laboratories. It should therefore be carefully investigated whether the lower yield with this process as recorded by Mahood is due to destruction of cellulose substance on account of excessive chlorine treatment, or whether it is due to a less complete purification with Schorger's equipment.

HAMMERMILL PAPER COMPANY
ERIE, PENNSYLVANIA
November 5, 1920

BJARNE JOHNSEN

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

Johnsen contends that my conclusions "are based upon insufficient analytical data and upon statements that are misleading and partly incorrect." It is to be regretted that Johnsen offers no new experimental data in support of this rather sweeping statement.

The first point at issue concerns the definition of cellulose, and it is stated that I (in common with Dore) am "inclined to regard as cellulose all substances in the cellulose residue which do not give furfural reaction." This statement is indeed misleading, for, in regard to the cellulose obtained in the investigation under discussion, I say that "the cellulose obtained in each case was treated with chlorine and sodium sulfite to the point where no color was obtained." This defines wood cellulose as well as our present knowledge of its chemistry will permit. The residue thus obtained is made up apparently of hexosans, pentosans, and possibly furfural-yielding constituents other than pentosans. Johnsen's original paper on the subject, as well as his more recent discussion of it, is open to the criticism that he does not define what he means by cellulose. Apparently he considers that there is but one cellulose, and that normal or cotton cellulose. As pointed out by Schorger, it is no more reasonable to expect cotton to be the only cellulose in nature than glucose to be the only sugar. It is probable that wood celluloses should be looked upon as definite compounds of hexosans with varying amounts of pentosans.

¹ *Z. angew. Chem.*, March 5 and 12 (1918); *Paper*, 23 (1918), 277.

¹ *Loc. cit.*

We are not obliged to assume, as Johnsen contends, "the presence in wood of hexosans of less resistance than cellulose and which can therefore be separated from cellulose by hydrolysis, but by a more effective hydrolysis than that obtained by sodium sulfite at 100° C." This assumption is very convenient for the purpose of correlating Johnsen and Hovey's method of cellulose determination with the wood pulping processes, but it ought to have some experimental basis which as yet is entirely lacking. Commercial processes are as a rule poor criteria by which to judge analytical methods. It is generally considered that the difference between the yield of cellulose obtained from wood by the laboratory method and that obtained by the pulping processes is due to the more drastic treatment in the latter which destroys some of the cellulose. Since Johnsen and Hovey's method gives a "residue more identical with the pulps obtainable in the commercial processes" it may be assumed, in the absence of experimental data to the contrary, that it, too, destroys some of the cellulose.

Johnsen objects to my statement that "approximately the same result could be attained by a further chlorination of the sample than usual" in reference to the residues obtained by his method. Approximately 50 per cent of the furfural-yielding constituents of woods are removed by the chlorination process. It seems reasonable to suppose, therefore, that a further loss of these constituents would result on continued chlorination (Johnsen says "this is not so," but gives nothing to show that it is not). Since it is not permissible, as Johnsen points out, to continue chlorination after the total lignin has been removed, as this would result in oxidation of the cellulose, further chlorination of the sample than usual would have the effect of reducing both the pentosan and the pentosan-free cellulose content, and this is the apparent effect of the digestion with glycerol and acetic acid.

Johnsen's statement that my criticism of his method is based "to a very considerable extent on Dore's experiments" seems to be an attempt at subterfuge. My data show that the yield of pentosan-free cellulose as well as the pentosan content of the cellulose is reduced by preliminary treatment of the wood sample with the acetic acid-glycerol mixture. Johnsen explains this lowering of the pentosan-free cellulose by assuming that the loss is due to hexosans less resistant than cellulose, but there is nothing in Johnsen's paper to warrant this assumption. On the other hand, Dore's data corroborate mine, and although it is true that laundering, beyond a certain point, reduces the resistance of cellulose, the data still hold for the comparative purpose for which they were intended.

Johnsen's observation that "two statements" in my article "are in disagreement with the results of other investigators" should be modified to include only two other investigators, *i. e.*, Sieber and Walter working jointly, and it should be noted that my statement in regard to the effect of temperature is supported by Cross and Bevan and by the work of Renker.

The fact that my data are not in accord with those of Sieber and Walter on the loss in weight of the fibrous pad emphasizes this potential source of error in the procedure. I used the best calico obtainable and subjected it to treatment with chlorine and sodium sulfite prior to making the test runs. The loss entailed will be determined largely by the previous history of the calico, and since this cannot usually be determined it cannot be assumed that the loss in weight will be negligible if accurate results are desired. If other objections to the Sieber and Walter procedure are overcome this potential source of error can probably be eliminated by the use of a Willard crucible.¹

Applying Johnsen's test of purity of cellulose, *i. e.*, the amount of furfural it yields, to the cellulose residues obtained by me with Sieber and Walter's apparatus, they contain an average of 7.68

per cent pentosan, while those obtained with Schorger's apparatus contain 7.35 per cent. The purity of the residues, which Johnsen thinks may be different, appears, therefore, to be of the same order.

The lower yield of cellulose using Sieber and Walter's equipment does not appear to be due to "excessive chlorine treatment," as indicated by the following data from my paper:¹ "Five one-half hour chlorinations were required for complete chlorination following Cross and Bevan's procedure while periods of 20, 15, 15, 10, and 10 min. were required with the modified procedure." Taking into consideration these experimental facts and also the work of Cross and Bevan and of Renker, my statement that "the higher yield (of cellulose) obtained using the original procedure, notwithstanding the longer exposure to chlorine, is probably accounted for by a lower concentration of chlorine and a lower chlorination temperature" seems justified.

In the hands of competent analysts the mechanical losses in manipulation using the method of Renker and of Schorger are negligible. The only advantage of the Sieber and Walter method is a shortening of the time required for the analysis. With the use of the Willard crucible, a dilution of the stream of chlorine or the use of a suitable cooling device or both of these, perhaps, it may be made to give as good results as the original Cross and Bevan procedure.

The statement by Johnsen that the Sieber and Walter method "has been adopted by most of the recent investigators and by commercial laboratories" is answered in part at least by the following from the article by Johnsen and Hovey:² "As in recent investigations use has not been made of this improvement, which in our opinion is extremely valuable, the preparation of the crucible as suggested by Sieber and Walter is described here." Where it has been used it apparently has been adopted in the way that Johnsen and Hovey adopted it, *i. e.*, without determining its accuracy in comparison with the original procedure. Johnsen's suggestion that the controverted points should be "more thoroughly investigated" is therefore timely. In this investigation should be included another of Sieber and Walter's conclusions as stated by Johnsen "that four chlorinations with a total exposure to the gas of 1 hr. was sufficient for the complete removal of the lignin from wood." Schorger³ found the number of chlorinations necessary to obtain lignin-free cellulose to vary with wood from the same species as well as with wood from different species.

Up to the present time the Johnsen and Hovey method has not proved to be "a standard method which could be recommended for future investigations." In fact, with the determination of the furfural-yielding constituents as the sole test of purity of the resulting cellulose, the treatment with the glycerol-acetic acid mixture, in addition to being objectionable for reasons already pointed out, seems superfluous, since the percentage of cellulose free from furfural-yielding constituents or "pure" cellulose can be obtained by deducting the percentage of these "impurities" from the cellulose values obtained by chlorination. Such a correction is recommended by Schwalbe⁴ and is made by him and Becker⁵ recently in the analyses of some species of German woods. It can be applied to the results of Schorger and others who have recorded the pentosan content of the cellulose if one objects to furfural-yielding constituents as impurities in the cellulose.

THE LABORATORY OF ORGANIC CHEMISTRY
TULANE UNIVERSITY, NEW ORLEANS, LA.
February 8, 1921

S. A. MAHOOD

¹ THIS JOURNAL, 12 (1920), 875.

² J. Soc. Chem. Ind., 37 (1918), 133t.

³ THIS JOURNAL, 9 (1917), 563.

⁴ J. Soc. Chem. Ind., 37 (1918), 132t.

⁵ Z. angew. Chem., 32 (1919), 125.

⁶ Ibid., 32 (1919), 229.

¹ Described at the St. Louis Meeting of the American Chemical Society, April 12 to 16, 1920. The bowl of this crucible is pyrex glass, while the bottom consists of a porous alundum disk which is fused to the glass.

Editor of the Journal of Industrial and Engineering Chemistry:

Johnsen protests against my statement that "all processes [for the determination of cellulose in woods] involving preliminary hydrolysis result in a diminished yield of α -cellulose as well as total cellulose and are therefore unacceptable as accurate cellulose processes." This, he maintains, I have failed to prove "by convincing experimental data."

The first part of the above statement is nothing more than the verbal expression of data which Johnsen has quoted in Table II, and may be regarded, therefore, as a fact beyond dispute if the data be accepted as reliable. The second part of my statement deals with the significance and interpretation of these facts and it is with this part that Johnsen's criticisms are concerned.

Johnsen expresses a doubt as to whether α -cellulose is a well-defined substance, inasmuch as that obtained from Renker's process yields an average of 0.50 per cent furfural while that from the Johnsen and Hovey process yields only 0.26 per cent furfural. The differences in furfural yield do not necessarily indicate that the α -cellulose is an ill-defined product. It is by no means certain that the furfural obtained from the α -cellulose residues is due to pentosans; on the contrary, the fact that the yield is small increases the probability that it originated in other substances, for it is well known that other carbohydrates than pentosans are capable of yielding furfural, usually, however, in but small amounts. Furthermore, the fact that the amount of furfural obtained from any one substance varies according to the conditions maintained during the analysis appears to indicate that the furfural is obtained, not altogether from pre-formed groups, but, at least in part, by rearrangements within the molecule. In view of the known labile character of the cellulose molecule, it is not unreasonable to regard the furfural yield of the α -cellulose as probably resulting from such rearrangement. The observed differences in furfural yield between the α -cellulose residues by the two processes may be due to alterations in the molecular arrangements during preliminary treatment. Such changes may be assumed to take place without necessarily implying that the two products are essentially different.

Since the furfural yield is subject to the influence of so many possible factors, it would appear that the conclusion expressed in my original article is correct and that no significance is to be attached to the small furfural yield of the α -cellulose.

Johnsen claims that the α -cellulose by the Johnsen and Hovey process yields an amount of furfural approximating that from purified cotton. This claim is based upon the agreement of data which are not properly comparable. The figures quoted in Table III of Johnsen's article show that the residue by the Johnsen and Hovey process yields 0.26 per cent of furfural expressed in percentage of the original air-dry wood. When recalculated to the basis of the α -cellulose, which constitutes 34.64 per cent of the air-dry wood, the furfural yield by the Johnsen and Hovey process becomes 0.75 per cent. When this figure is compared with that given by Johnsen for the furfural yield of purified cellulose (0.24 per cent), it is clear that the residue by the Johnsen and Hovey process yields considerably more furfural than purified cotton.

Inasmuch as it is generally recognized that substances other than pentosans are capable of yielding furfural, we are not obliged either to assume or disprove that the furfural yield of cellulose residues is due to pentosans. It appears probable that the small yields of furfural from the α -cellulose residues are largely or wholly due to other sources; therefore Johnsen is not justified in assuming that the furfural originates in pentosans, or in applying a pentosan correction to the residue. He has accordingly failed to disprove that the total cellulose and α -cellulose are "destroyed in the same proportion."

The data in the last column of Table II, quoted by Johnsen, show that the total cellulose by the Renker process contains an average of 75 per cent of α -cellulose, while that by the Johnsen

and Hovey method contains an average of 78 per cent of α -cellulose. In the case of cotton cellulose, the total cellulose by the Renker process yielded 95 per cent of its weight of α -cellulose, and that by the Johnsen and Hovey process yielded 94 per cent of α -cellulose. This is apparent from the following data quoted from Table IV of my original article:¹

TREATMENT	Total Cellulose	α -Cellulose	Ratio α -Cellulose: Total Cellulose
No hydrolysis (Renker's method).....	89.90	80.32	0.95
Acetic acid and glycerol 4 hrs. at 135° C. (Johnsen and Hovey's method).....	85.91	80.63	0.94

My original contention, in so far as it applied to the Johnsen and Hovey process, was that the differences between 75 and 78 per cent in one instance, and between 95 and 94 per cent in another, are not sufficient to indicate a material improvement in the purity of the product by the Johnsen and Hovey process over that by the Renker process. It therefore appears correct to ascribe the diminished yields of total cellulose and α -cellulose to a destruction of those substances in practically the same proportion.

Johnsen has shown that if the furfural of the α -cellulose be calculated to pentosan and deducted, the residue by the Johnsen and Hovey process still contains 1.58 per cent less of the pentosan-free α -cellulose than the residue by the Renker process. This difference, he maintains, is probably due, not to an attack on normal cellulose, but to a removal of less resistant carbohydrates not properly to be regarded as cellulose. However, these carbohydrates, which Johnsen would exclude from the α -cellulose residue as not being normal cellulose, are resistant to chlorination and sulfite treatments and the subsequent treatment with 17.5 per cent sodium hydroxide. It would seem, therefore, that there is little or no justification for designating them as "lower carbohydrates," or classifying them with the hemicelluloses when their properties are so much more closely related to those of the true celluloses.

In my original article² my conception of cellulose "as applied to material derived from woods," was stated as the "residue remaining after alternate treatments with chlorine and sodium sulfite solution" when the process is "preceded with non-hydrolyzing treatments only. The residue so obtained should be free of lignin and hemicelluloses. It may contain α -, β -, and γ -celluloses corresponding to the definitions of those substances implied by the conditions of the mercerization test, also furfural-yielding complexes, but should be free from easily hydrolyzable pentosans." The quotations should render unnecessary any speculation as to what I consider cellulose.

The definition of cellulose as a residue of processes is consistent with the views of Cross and Bevan and those of Renker. Schorger, who confirmed some of Renker's views, has given a formal definition of cellulose as "the residue remaining after alternate treatment with chlorine gas and sodium sulfite up to the point where the chlorine sulfite color reaction or the Maule reaction disappears."³ All of these authors regard cellulose as a residue of processes. Until more complete information exists regarding its chemical nature, it appears desirable to regard wood cellulose as a group of substances with a similar degree of resistance to reagents. Repeated attempts to narrow it down to a single substance, similar to the cellulose of cotton, have been uniformly unsuccessful, because the high resistance of the residue requires the use of drastic reagents, which invariably attack all members of the group.

Johnsen claims that my statement that "the hydrolytic processes do not remove any appreciable amount of the furfural-yielding complexes from the product" is not supported by experimental data. The data quoted in Table III show that the

¹ THIS JOURNAL, 12 (1920), 268.

² Loc. cit., p. 269.

³ THIS JOURNAL, 9 (1917), 563.

total cellulose by Johnsen and Hovey's method yields only 0.33 per cent less furfural than that by Renker's process. The same table shows a variation of 0.33 per cent between the highest and lowest of four determinations of furfural yield on material prepared by Renker's process. No significance can be attached, therefore, to a diminution of a few tenths of 1 per cent in furfural yield, and the results indicate that at most only a trifling reduction in furfural yield is accomplished by the Johnsen and Hovey method.

It is claimed for the Johnsen and Hovey method that it gives a residue corresponding closely to that obtained in manufacturing wood pulp, and that it is therefore "very useful in the valuation of woods for the commercial paper pulp processes." I do not dispute the possible value of this method as a technical method in pulp mill practice. The residue, however, does not conform to any recognized conception of cellulose and should not be so designated. Johnsen does not claim that the residue by the Johnsen and Hovey process is "pure" in the same sense that he regards the Renker residue as "impure." He claims that the former is purer, but the most favorable data show that at best it can be regarded as only slightly purer. Furthermore, the reduced yields of total and α -cellulose by the process show that true cellulose is partly destroyed. (This statement rests upon the experimental data which Johnsen has quoted. It has been questioned by him but not disproved.) It is my contention, therefore, that however useful the Johnsen and Hovey method may be for judging the paper-making qualities of woods, it is unsuitable for scientific investigations on the chemical nature of woods or other cellulosic materials.

Johnsen has taken exception to my statement that "cotton sheeting which had been repeatedly laundered" might be considered "a residue of highly resistant cellulose mostly of the normal type." The fact that the residue on chlorination yielded 95 per cent of α -cellulose shows both a high degree of resistance and a high proportion of α - or normal cellulose. No claim has been made that it was in any sense a chemically pure cellulose, and it was not necessary that it should be such for the purpose in mind, namely, to determine whether cellulose from an unglified source showed the same behavior as wood cellulose. The data show that this cellulose, as well as wood cellulose, gives less total and less α -cellulose when treated by the Johnsen and Hovey method. The reduced yields of α -cellulose indicate that the normal cellulose is attacked by this process.

Experiments with highly purified cellulose are undoubtedly capable of contributing greatly to our knowledge of fundamental cellulose chemistry. It is unfortunate that the valuable data to which Johnsen has referred have not been published in detail, and it is to be hoped that they soon will be made completely available.

WALTER H. DORE

UNIVERSITY OF CALIFORNIA EXPERIMENT STATION
BERKELEY, CALIFORNIA
January 31, 1921

Phthalic Anhydride Derivatives

Editor of the Journal of Industrial and Engineering Chemistry:

I noted with interest the list of phthalic anhydride derivatives appearing in THIS JOURNAL, 13 (1921), 274. I was surprised to note that some of the commercially most important derivatives have been omitted. I am listing below certain of these products and the literature references for the same, and suggest that these be added to the list already published.

Naphthoyl benzoic acid
Naphthanthraquinone

Schultz' "Dyestuff Tables," 260. Also, under the dyestuffs should be added the product known and sold as Sirius Yellow G, which is produced from the above-mentioned intermediates, and is an important dyestuff in the lake pigment industry.

Anthraquinone
 α -Benzoylbenzoic acid

Z. angew. Chem., 19 (1906), 669; *Ber.*, 41 (1908), 3631

Quinizarin (1,4-Dihydroxy-anthraquinone)

Ber., 6 (1873), 508; U. S. Patent 708,142. This product is used in the production of two very important dyestuffs, namely, Alizarin and Cyanine Green, and Alizarin Direct Violet, also known as Alizarin Irisol

2-Methylantraquinone

Ber., 41 (1908), 3632. This very important intermediate is used in the manufacture of three well-known vat dyes, namely, Anthraflavone G, Cibacene Orange R, and Cyananthrol R and G. This last-named intermediate is used in the production of other intermediates, from which are produced other vat dyes such as, for example, Indanthrene Gold Orange G

Hydron Yellow

D. R. P. 1,055,287

A very good reference on all the above-mentioned products may be found in "The Manufacture of Intermediate Products for Dyes," by J. C. Cain, 2nd Ed., Macmillan & Co., 1919.

You may see from the above list, which is by no means complete, that there are some very important products among them, from the standpoint that they are the starting points for the manufacture of dyestuffs, a great proportion of which have not as yet been produced in this country.

THE CHEMICAL FOUNDATION, INC.
81 FULTON ST., NEW YORK, N. Y.
March 5, 1921

ARTHUR LINZ

A Memorial of Sir William Ramsay

It has just been learned that the Dean and Chapter of Westminster Abbey have decided to place a bronze medallion in the Abbey as a memorial of Sir William Ramsay.

The news of this tribute to the genius of the brilliant English chemist will be received with the deepest and most sympathetic interest among his many American friends, who regarded him so highly as a scientist and loved him so truly as a man.

Federal Trade Commission Rulings

The Federal Trade Commission has denied the application of the Meadows Oil and Chemical Corporation for license under the Trading-with-the-Enemy Act to use trade-marks covering ichthylol. A former application made in November 1920 was denied, but the company applied for a re-hearing, which took place on January 25. The Commission says "it is not to the public interest to grant the desired license." Last December the War Trade Board called the company's attention to the fact that a bulletin issued by the company regarding importations of ichthylol had been so worded as to mislead a number of firms into thinking it an official statement of the War Trade Board. The Meadows Company has issued a statement explaining that this impression was not intentionally created. According to a statement by the Board, "Information received by the War Trade Board would tend to show that American ammonium-ichthylol-sulfonate and other substitutes for German ichthylol—satisfactory physically, chemically, and therapeutically—are obtainable from domestic sources on reasonable terms as to price, quality, and delivery. It is understood, of course, that the American product is not derived from the bituminous shale found in Seefeld, Tyrol, but is derived from a somewhat similar fossiliferous rock found in Texas. Any statements which we may make regarding the issuance of licenses to import German ichthylol are subject to revision upon the receipt of new information which may tend to prove that the American product is or is not a satisfactory substitute in all respects for the German ichthylol."

The Commission has cited the Winthrop Chemical Company, Inc., New York City, in complaint of unfair competition in the drug trade. The company is charged with falsely advertising that genuine veronal is sold exclusively by that company. Prior to the war veronal was sold in the United States under a German patent, and during the war three American manufacturers, not including the Winthrop Chemical Co., were licensed by the Federal Trade Commission to make and sell veronal. Subsequently the Winthrop Company bought from the Alien Property Custodian the German trade-mark with the right to make and sell veronal. April 12, 1921, or shortly thereafter has been set for the hearing of the complaint.

WASHINGTON LETTER

By WATSON DAVIS, 1418 Rhode Island Ave., Washington, D. C.

The new administration is now passing through its first days of power, and these are times of conferences and meetings on Capitol Hill, at the White House, and in the various departments. Tariff and appropriation legislation programs are being formulated in anticipation of the convening of Congress on April 11, as President Harding announced only this afternoon.

PLANS FOR THE TARIFF BILL

Following a conference this afternoon of Republican members of the Senate Finance Committee and the House Ways and Means Committee with Secretary of the Treasury Mellon and his advisors, it was decided that a permanent tariff bill will be drafted at once and that no attempt will be made to push through an emergency tariff. Whether tariff or revenue bills will come first, or whether they will be considered concurrently, is still undecided.

The dye and the chemical industries in general will be amply protected in the complete revision of the tariff that will be made, is the assurance of Representative Nicholas Longworth, who will probably head the Ways and Means Subcommittee on Schedule A, chemicals. That these essential chemical industries should have protection from foreign dumping is the unanimous opinion of those who will frame the necessary legislation, it is said. The decision for a permanent tariff bill means more hearings, and it may be weeks and months after the convening of Congress before the final bill is signed. Values and rates in the Fordney Emergency Tariff Bill that was not passed over President Wilson's veto will exert little influence on the new legislation.

The decision reached at to-day's conference, that an anti-dumping bill and a measure providing for the levying of ad valorem duties on the domestic valuation instead of on the foreign basis of valuation, as at present, will be rushed through both houses, is of vital interest and importance to the chemical industry. These two measures will be designed to give emergency protection to American industry, the former by preventing foreign dumping of goods and products in this country at prices below the cost of production, and the latter by eliminating the advantage given to foreign goods by reason of the present exchange situation.

THE CHEMICAL WARFARE SERVICE

That the position of the Chemical Warfare Service will be very secure and that the present administration will give favorable consideration to chemical warfare, is the statement of Senator Wadsworth, chairman of the Military Affairs Committee. While it probably will not be possible to give this branch all the money it asks for, the fundamental and important research and development connected with gas warfare work will be aided and pushed, according to Senator Wadsworth. This view of the importance of chemical warfare is in contrast to that held by the retiring Secretary of War and Chief of Staff who opposed the organization of that Service as a separate unit.

According to Gen. Fries, Secretary of War Weeks is very favorable to the Service and appreciates its importance. The Army Appropriation Bill which received a pocket-veto by President Wilson gave \$1,500,000 to the Service, instead of the \$4,500,000 asked for, and Gen. Fries states that plans are being made to continue the research, development, and proving of gases and masks and other material, and to cut down plant maintenance and supplies, with the expectation that the million and a half appropriation will be made in the new army bill.

GOVERNMENT REORGANIZATION

Government reorganization is one of the first items on the program of President Harding and his cabinet. The Joint Congressional Commission headed by Senator Smoot is considering this problem. The backbone of the reorganization scheme is said to be the adoption of the national budget system, the reorganization of the departments according to a systematic and logical plan, and the effecting of personnel and salary changes along the lines recommended by the joint commission on reclassification. How the chemical and research bureaus of the departments, and the government chemists, will fare is problematical. It has been proposed that all of the bureaus concerned with educational and scientific research work should be grouped under a new department of education and science. The Public Works plan for grouping the engineering agencies, which has been definitely outlined in the Jones-Reavis Bill, will receive early consideration, it is said.

The Nolan Patent Bill was not voted on in the Senate after being in conference and was therefore defeated. It is ex-

pected that the three important portions of the bill, the salary and reorganization features, the provision for the taking over and administration of patents by the Federal Trade Commission, and the amending of statutes dealing with patent litigations, will be reintroduced as separate bills at the coming session. Senator Norris, present chairman of the Patent Committee, will become chairman of the Committee on Agriculture and will probably be succeeded by Senator Brandegee. Representative Nolan will probably be made chairman of the House Labor Committee, while Representative Lampert will probably head the Patent Committee.

The appropriation of \$10,000,000 for the completion of Wilson Dam of the Muscle Shoals Power Plant was lost when the Senate receded and passed the Sundry Civil Bill without the amendment. When this action on the nitrate plant proposition was taken, the Chief of Engineers instructed that all further construction work be stopped, and there is, at present, about \$1,000,000 left, which will be sufficient for maintenance work until such time as final decision is made as to the fate of the entire project at Muscle Shoals.

The appointment of Herbert Hoover to be the Secretary of Commerce in President Harding's cabinet is one of the most important features in the change of administrations from the standpoint of the technical man. Mr. Hoover has taken up the task of making the Department of Commerce more beneficial to the country. While he has announced that radical changes in the scope of the department's activities will await the general governmental reorganization, his ideas for immediate activity include: Better coöperation between industry and the foreign agents of the Bureau of Foreign and Domestic Commerce; constructive study of transportation; power development and labor readjustment; extension of voluntary standardization of manufactured products; promotion of greater efficiency in industry; applying idle labor to such needed projects as housing, power plant development, waterways, and highways.

NATIONAL RESEARCH COUNCIL

The National Research Council Division of Chemistry under Dr. F. G. Cottrell is coöperating with Prof. W. L. Badger of the University of Michigan in his work on boiling points of saturated solutions under various pressures. As a result, the work that he is doing for commercial organizations, on the theory and heat transference of evaporators, will be carried to a higher degree of accuracy than is necessary for the primary object of the tests.

While the organization of the Alloys Research Association is not being vigorously pushed by the National Research Council at the present time on account of the industrial situation, a considerable number of large metallurgical firms have joined.

DR. ALSBERG RETIRES FROM BUREAU OF CHEMISTRY

To assume directorship of the Food Research Institute that the Carnegie Corporation will establish at Leland Stanford Junior University, Dr. C. L. Alsberg will leave his present position as chief of the Bureau of Chemistry of the Department of Agriculture about June 1. It is understood that politics will not enter into the selection of Dr. Alsberg's successor, but that the best chemist obtainable for the position will be appointed.

An appropriation of \$25,000 has been given the Bureau of Chemistry to continue its investigations of explosive and inflammable dusts that are a menace in mills, elevators, oil-presses, gins, and other places where dust is created. With the idea of transferring its appropriation for fish and sea food investigation to the Bureau of Fisheries, the Bureau of Chemistry's appropriations for this activity were cut off. However, as no money was given the Bureau of Fisheries, these investigations must be suspended.

A chemist and a college professor entered the Senate when Dr. Edwin F. Ladd took his seat as a senator from North Dakota. He has been for years president of the North Dakota Agricultural College.

Dr. E. D. Ball, who is professor of entomology and zoölogy at Iowa State College and state entomologist of Iowa, has been reappointed Assistant Secretary of Agriculture to continue the general direction of the department's scientific work.

March 14, 1921

LONDON LETTER

By STEPHEN MIALI, 28, Belsize Grove, Hampstead, N. W. 3, England

THE EXCESS PROFITS DUTY

In the dark and gloomy sky which overshadows all, a small patch of blue has just made its appearance, the abolition of the Excess Profits Duty.

The abolition of this obnoxious duty fills us all with hope and gives us a certain modified confidence that the present lack of trade is teaching us a much-needed lesson. But it will not do very much more than this; the causes of the present unemployment are so deep seated, so varied and so interdependent that a great lapse of time, much patience, and the wisest of counsels will be required to make the necessary change. I see no reason to think that in three, six, or twelve months trade will be what it was a year ago. How long will it be before Russia can again buy huge quantities of tea from India and so enable India to buy goods from England? When will Austria and Germany, Czechoslovakia and Poland, buy from France and Italy? Some day Greece and Turkey will convert their swords into ploughshares, the Sinn Fein will lie down with the Ulsterman, and the suspicion which suggests to Britain, America, and Japan a naval rivalry will be replaced by a desire for coöperation to advance the happiness of the world. Until those days come the world trade on which we all live will not really flourish. But we are getting nearer to that time every day, and we have turned the corner. Business is not quite so stagnant as it was in December; but up to now the big firms here have weathered the storm, so they will repair their shattered barks, untaught and unwilling to endure poverty.

Conservation of matter, conservation of energy, have had their day; conservation of resources is now the watchword, and accordingly the developments in industrial chemistry are meager. They are like the Irishman's crop of potatoes which did not come to as much as he expected, and he never thought they would. Although many commodities have not yet reached their bottom price, some few seem already to have done so. Moreover, the stocks in the hands of merchants and retailers are slowly getting exhausted, and the orders for which we are waiting seem to be gradually preparing to emerge from their present obscurity.

THE DYESTUFFS BILL

The Dyestuffs Bill has, in spite of opposition and even obstruction, found a place on the Statute Book. Naturally a bill of this description revived to a small extent the old Free Trade or Protection controversy. The advocates of cheap goods flourish in Lancashire and other parts of England, and they would have been able to put up a very strenuous fight had not the circumstances of this bill been so unusual. Its supporters urged that an aniline dye industry is an essential part of that chemical trade without which no country can be a great industrial power; that an aniline dye industry is a necessary part of our national defense as the only industry in which poison gases of modern type can be speedily made in large quantities; and, lastly, that protection to the industry had been definitely promised by this and the preceding Governments. These arguments are really unanswerable and do not concern the question of Free Trade or tariffs. But a determined fight was put up by the Labor party and a band of vigorous Free Traders who feared that expensive dyestuffs would kill the textile trade of Yorkshire and Lancashire and urged that the Government could keep its promise by giving a subsidy for the promotion of research on dyestuffs and their cheaper manufacture. As to the necessity of cheap dyestuffs, all were united, and it was argued that in the long run it would pay to keep up some manufacture here to prevent the Germans from obtaining a monopoly and then raising the prices, as was done to a certain extent in pre-war days in the alizarin dyes. Also the bill only proposed to restrict foreign imports by the agency of a licensing committee on which the consumers were adequately represented. The alternative of restricting imports or granting a subsidy was hotly debated in the Press and in Parliament. Many over here, including myself, prefer in general the granting of a subsidy as being more effective and more economical. From the point of view of the direction of money to the place where it is needed a subsidy is quicker, simpler, and more easily controlled. But in this especial case the difficulties surrounding a subsidy to the dyestuff industry were colossal. Britain, France, Belgium, and some other European countries were receiving from Germany considerable quantities of dyes under the treaty of peace. All these countries were receiving more than there was a demand for, and most

of them were selling their surplus in this country. The consequence was that at the end of 1920 there lay in warehouses in England nearly enough German dyes to supply the whole consumption for 1921. Had the importation not been stopped, the subsidy necessary to keep the British works progressive and usefully employed in manufacture and research would have been enormous.

MANUFACTURE OF FINE CHEMICALS

Similar arguments will arise again in this country pretty shortly. There is talk of introducing a bill for the protection of the fine chemical manufacture and, in particular, the manufacture of synthetic drugs. It is by no means certain that such a bill will be so acceptable as the Dyestuffs Bill. Many of the special arguments in support of the latter do not apply to the manufacture of fine chemicals. Moreover, the fine-chemical manufacturers have not hitherto made the opportunity or the organization to render to the community services comparable to those rendered by the dye makers. Broadly speaking, fine chemicals have here been made by small firms with either insufficient ambition or insufficient capital to create that large enterprise necessary to supply this country with a wide range of fine chemicals and research reagents of guaranteed purity. Whether this is now the occasion and whether—assuming it to be such—it will be seized, no one can say. The Dyestuffs Bill is no precedent.

But our Free Trade arguments will be put to the proof in connection with the German indemnity. How much we shall get and in what shape it will come seem to me minor matters in comparison with the great question: Will it do us any good to get an indemnity? I suppose Germany has a small quantity of gold, but not enough to count where thousands of millions are involved. Now that she has lost Alsace and Lorraine and undertaken to send to France coal to replace the supply from the French coalfields so stupidly destroyed by the Germans, she has not an enormous surplus of raw materials to export, or of foodstuffs. We have taken her ships and incidentally caused short time in English shipyards. So if she pays at all, it looks as if she will pay in manufactured goods. Now, in old days, if we took £20,000,000 of goods from Germany we paid for it by sending out to her (or some other country) £20,000,000 of British-made goods, and employment was not affected. If we are going to receive, without sending anything in exchange, some huge quantities of German manufactured goods, shall we not increase the unemployment already terrible enough here? After the Franco-Prussian war it was Prussia, not France, which had a slump in trade. To reconcile war and its consequences, including revolutions, indemnities, depreciation of currency, and so on, with trade and the pursuit of money is a hopeless task and reminds one of a schoolboy with an axe, a glue pot and some fireworks, trying to regulate an eight-day clock. Whatever he does he will spoil the mechanism and one must be thankful if he comes away without the flash, bang, and sting, which are the marks of what juvenile students consider a successful chemical experiment.

February 14, 1921

.....

This morning we cannot help considering the meaning of the break in the negotiations between the Allies and Germany and its effect on the economics of the world. It is apparently as difficult for us to understand the German mentality and diplomatic methods as it is for them to understand ours. It is singular that two peoples, each partially descended from the same stock and speaking varieties of the same Teutonic language, having had much intercourse both social and commercial in the past, should in the space of a few years have drifted so much apart that one is quite unable to understand the point of view of the other. It will require a good deal of care to prevent the same catastrophe from dividing the great English-speaking nations of the two sides of the Atlantic, and that is why the meeting of their chemists in Montreal and New York this summer is of such infinite importance. It is chiefly the trifling matters of divergence which are so difficult to adjust, but it is these which become of greater and greater importance. I think I notice a tendency towards a greater divergence in our language than existed thirty or fifty years ago; unless we are careful we shall in time become mutually unintelligible. Cannot we chemists take a step toward greater community of ex-

pression? It will be hard for either side to give up the little tricks and prejudices which are our pride. But is not the permanent community of thought worth this small sacrifice? It is perhaps too early in our history to suggest that to prevent undue divergence a joint committee be appointed to consider our scientific or at any rate our chemical language?

KEY INDUSTRIES BILL

The details of the new Key Industries Bill, which is to protect the manufacturers of fine chemicals, optical glass, scientific

instruments, magnetos, and other things, are not yet published, and one hears rumors that the advocates of tariffs and the advocates of importation under licenses are unable to agree upon a common policy. The makers of fine chemicals favor importation under a system of licenses such as prevails in the dyestuff industry, but the application of this principle to all the objects in the schedule of the Key Industries Bill would be extremely difficult and cumbersome. Recent bye-elections here do not point to any considerable departure from free trade.

March 8, 1921

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

THE CLAUDE PROCESS

The importance of the nitrogen problem leads me to report to you each month new developments which have occurred along this line.

Mr. Georges Claude is steadily developing his process and expects it to supersede the Haber process. He has just constructed a hypercompressor of greatly reduced dimensions. This apparatus will compress 700 cubic meters of mixed nitrogen and hydrogen per hour, thus yielding 5 tons of anhydrous ammonia, equivalent to 25 tons of ammonium sulfate per day.

This hypercompressor operates in two stages, the one at 100 to 300 atmospheres, the other at 300 to 900 atmospheres, the pressure finally used. For an output of 710 cubic meters per hour compressed from 100 to 900 atmospheres, the electric current is 97 kw., and the mechanical power 122 h. p. The total power from 1 to 900 atmospheres is 310 h. p.

Numerous tests have verified these figures, and in spite of the high pressures, the total leakage is only 3 cubic meters, or 0.5 per cent.

All preliminary calculations had pointed to this result, but the realization is now accomplished, and the process seems to be definitely perfected. There remains only one further problem, the feeding of the hydrogen. Mr. Claude has undertaken the study of this question.

A company with an initial capitalization of one million, to be increased soon to ten millions, has been formed in Italy for the development of the Claude process. This company has been formed with the support of the Société de l'Air Liquide et des Produits Chimiques de Saint Gobain.

DYE MANUFACTURES

The Compagnie Nationale des Matières Colorantes has just completed the development of basic dye manufacture, and is undertaking the manufacture of alizarin dyes. These two industries are established at the factory of Villers-St. Paul, near Creil. The old national powder mill at Oissel has been made over by the same company, which will make there the entire series of azo colors.

Similar efforts in the United States and in England lead us to hope that the dye market may soon be entirely free from German influence, although the German companies have enormously increased their capital and are trying to maintain their old supremacy.

During the war the German chemical industries also studied a number of industrial chemical problems for the replacement of natural products of which their country was deprived. Thus, they manufactured synthetic rubber, and also fat yeasts to replace feeding stuffs. The future of these industries seems very doubtful.

ALCOHOL MANUFACTURE

Among these industries rising from the war, that of alcohol derived from calcium carbide seems the only one worth continuing. At the last meeting of the Société de Chimie Industrielle, Mr. Georges Mignonnac discussed this industry, which is being conducted on a large scale only by one Swiss concern.

The acetylene from the calcium carbide is converted into acetic acid and ethylidene acetate, then reduced to alcohol. The cost of making the alcohol by one of the procedures employed, starting from the acetylene, would be about 0 fr. 60 per liter. Although this price is relatively low, it seems that in France the tendency is toward the development of fermentation alcohol, from corn and Jerusalem artichoke, or from cassava which is furnished in abundance by our African colonies.

There is also noticeable a tendency to investigation in the domain of agricultural industrial chemistry, that is, research

on the products obtained from the vegetable kingdom. In France we are following attentively the attempts to cultivate camphor in the United States. Similar plantings have been made in the south of France and in Algeria, but the first results have not been very encouraging. I have personally analyzed camphor trees from the region of Antibes, and their camphor content is nil.

The Office des matières premières is carrying out systematic investigations on the culture in Algeria and Morocco, but it is too early to learn the results. Moreover, the market for camphor seems to be growing less. The celluloid industry is growing smaller, because of the manufacture in France of a large number of products of the bakelite type. On account of their noninflammability, these products are replacing celluloid to a greater and greater degree.

The Bureau of Mines has recently published its report for 1920. On the whole, there has been a marked increase in production, in mineral fuels as well as ferrous minerals and other metals, and especially in salts (rock salt and potash).

Mr. Matignon has made a study of the industrial preparation of magnesium from the oxide or chloride, by reaction with calcium carbide. He has obtained satisfactory results in the laboratory. The difficulty in the way of industrial application lies in the use of a high temperature (1200°), a temperature at which oxygen and nitrogen react with magnesium. The use of an inert gas, argon for example, would solve the problem, which thus rests on the industrial production of this rare gas.

This opens up an interesting problem which I commend to American investigators.

The city of Paris plans to establish a radium institute, for which it has voted the credit necessary for the purchase of a gram of radium metal for hospital use. Madame Curie herself is about to start for the United States, and during her visit will receive a gift of one gram of radium for use in her research work. Funds for this purchase are now being raised in America by popular subscription. We are extremely proud of the welcome which American chemists are offering to her.

I would call attention to the invention by Messrs. Bernard and Baron of an apparatus for lighting and extinguishing gas burners in towns. This apparatus permits lighting and extinguishing all the burners of a sector by turning a single cock in the factory. From the point of view of diminution in labor this invention is an interesting development.

March 12, 1921

Gift to Dermatological Research Laboratories

According to recent newspaper accounts, the sum of \$500,000 has been given by Drs. Schamberg, Kolmer, and Raiziss to the Dermatological Research Laboratories of Philadelphia, for the support of medical research. This sum represents the profits received during the war from the sale of arsphenamine which was manufactured—first as a war-time necessity, and later as a licensed preparation—at the Dermatological Research Laboratories. Inasmuch as the drug, though manufactured under war-time conditions, was sold at one-third the pre-war price of salvarsan, the vastly greater toll collected by the German proprietors for the sale of salvarsan may readily be calculated.

INDUSTRIAL NOTES

The Industrial Potash Corporation has been chartered at Salt Lake City with \$30,000,000 capital to develop the alunite deposits in the Mount Baldy, Ohio, and Durkee districts.

The Federal Trade Commission has cited the International Paint and Oil Company, of Peoria, Ill., in complaint of unfair competition in the manufacture of a coal-tar distillate called "tar-pentine," which can be used for some of the same purposes as turpentine. The complaint states that the name "tar-pentine" so closely resembles turpentine that the public might be deceived.

The Federal Trade Commission has cited the United Chemical Products Corporation, Jersey City, N. J., in complaint of unfair competition in the manufacture and sale of dyestuffs and chemicals. The company is charged with paying out approximately 10 per cent of its entire yearly business in cash commissions to dyers and other employees of its customers to influence the purchase of its products.

In the effort to prevent the Kali Syndicate of Germany from reestablishing a monopoly in the potash industry in the United States, the State Department has refused to vize the passports of the directors of the company to enter the United States, inasmuch as the German syndicate will not agree not to attempt to reestablish its monopoly of the potash trade by long term contracts or by other means.

The Atlantic and Gulf Export Company, recently organized with a capitalization of \$2,000,000, has completed its organization. Over one hundred firms are estimated to be represented. 300,000 bbls. of rosin have been pledged for export purposes, and it is planned to send representatives to Germany, Austria, Belgium, Italy, South America, and other countries. Business will also be conducted in lumber, petroleum, meats, hides, and other commodities.

Sixty-nine per cent of the world's petroleum production in 1919 came from the United States. Of the world total of 544,885,000 bbls., the American output was 377,719,000, Mexico coming next with 87,073,000 bbls., and Russia being third with 5 per cent of the output.

Announcement is made by the Bureau of Standards that renewal 5d of the exhausted Standard Iron Sample C and renewal 10c of the exhausted Standard Bessemer Steel 0.4 Carbon are now ready for distribution with provisional certificates. The price of these standards is \$2.00 per 150 g., and samples will be shipped by parcel post C. O. D. upon application.

The question of prohibiting carbon black companies operating in the north Louisiana gas fields from using natural gas or of forcing them to curtail the use of gas has taken a new turn, due to the contemplated construction of a pipe-line system to connect New Orleans, Baton Rouge, Alexandria, and other centers of population with the Monroe gas district, and the proposed construction of electrical power plants near Monroe to generate current for distribution over a wide area. The capitalists interested in both the pipe line and the electrical current projects are ready to begin construction if the carbon plants are closed or curbed, but not otherwise. They contend that the carbon mills are destroying the gas fields by the excessive use of gas, and will hardly last for ten years, while under the proposed plans it is said that the supply of natural gas will last for fifty or one hundred years.

The Dow Chemical Company has announced the production in the Midland plant of ethylene glycol and dichloroacetic acid, which are now made for the first time in America. Both materials are made by new processes and are of exceptional purity, since they are not subject to the impurities which have always resulted from their manufacture by the older processes involving the use of chloral as an intermediate. Prices at present are high on account of limited production, but are already below the prices formerly charged for the German products and may be still further reduced if new uses can be found, making increased production possible.

The School of Technology of the College of the City of New York now offers courses extending over a period of five years and leading to degrees in chemical, civil, electrical, and mechanical engineering. During the first two years the work consists almost entirely of prescribed collegiate science subjects; during the third and fourth years, of strictly engineering subjects, so arranged that the student is eligible for the degree of Bachelor of Science; and during the fifth year, of purely advanced technical engineering subjects. The engineering subjects are given in identical courses in both the day and evening sessions.

Three men were injured by an explosion which wrecked the building occupied by the Keystone Metal Reduction Company, Cheswick, Pa., on March 5, 1921. The plant is one of the three radium-producing plants in the United States and turns out about one gram of radium a year, valued at \$120,000. The explosion was caused by the blowing up of an autoclave. The loss is estimated at \$10,000.

At the annual meeting of the National Aniline and Chemical Co., Inc., the following directors were elected: Wm. Hamlin Childs, Wm. H. Nichols, Wm. H. Nichols, Jr., Edward L. Pierce in place of C. S. Lutkins, H. Wigglesworth, T. M. Rianhard, F. M. Peters, and W. N. McIlravy. The remainder of the board was reelected.

The New York office of the Société Commerciale des Potasses d'Alsace has been opened at 25 W. 43rd St., New York City. Captain F. C. Dossert is director of the American Bureau, and will become general sales manager for the Société on the resignation of Mr. W. B. Howe, general manager of the Nitrate Agencies Company.

The U. S. Department of Agriculture has decided to establish a production unit at Fitzgerald, Ga., for the manufacture of sweet potato sirup. The process was worked out in the Bureau of Chemistry laboratories by Dr. H. C. Gore. The sirup is rich in sugar, of a fine brown color and highly palatable, and has been found valuable for baking, candy making, and table purposes. Questions as to the cost of commercial production and the market value as compared with cane, corn, and other sirups have yet to be determined before the commercial practicability of its manufacture can be recommended. Production is to be begun as soon as the machinery can be installed.

The boiler house and main retort building of the Irvington Experimental Plant of the International Coal Products Company, of Newark, N. J., was destroyed by fire on February 21, 1921, with damage estimated at \$100,000. The plant is being rebuilt as quickly as possible.

On March 3, 1921, the Bureau of Mines, resorting to a wartime measure which gives it control over all importations of explosives, requested the customs officials to hold up all shipments of detonators and to send samples to laboratories of the Bureau for tests. The detonators sent here by German manufacturers for use in ditch digging and stump blowing are said to be of such low grade as to constitute a serious danger, and this step was taken to prevent the Germans from flooding the country with the low-grade detonators.

A preliminary announcement by the Bureau of Crop Estimates places the aggregate production of beet and cane sugar in the United States during 1920 at 2,605,174,000 lbs., or 1,163,023 long tons, approximately 53 per cent more than the 1919 production. The production of beet sugar is figured at 991,000 tons, an increase of 27 per cent over the previous record production, which was in 1915.

The Chilean government has formulated laws which it is expected will lead to the establishment of a fine beet sugar industry. Premiums to be paid by the government in gold are provided for beet sugar production, extending over 10 to 15 yrs. Import duties are established in case of a drop in price, and sugar machinery is admitted free of charge. The new law applies only to manufacturers having their homes in Chile.

The production of German dyestuffs during the year 1920 amounted to 145,000 tons, the largest output in the history of the industry, the average yearly production before the war amounting to 135,000 tons. During the month of January 1921 the production reached 12,000 tons and during February 1921 reached 15,000 tons.

Discovery of what may prove to be a large deposit of alunite has been made in Texas. There are said to be six outcrops of the mineral, from six to twelve miles apart, the outcrop of the higher grade variety covering approximately 20 acres and being of better quality than any other yet discovered in the United States. Samples have been tested by Mr. Braun, the discoverer, and also in the El Paso School of Mines, the University of Texas, and the San Antonio Public Service Co., and it has been demonstrated that the mineral is of the purest grade obtainable and means much to the country if it exists in quantities sufficient to warrant commercial exploitation. The fact that the alunite is found in a level country upsets the theory heretofore held by geologists that the mineral exists only in volcanic formation.

PERSONAL NOTES

Dr. J. C. Cain, editor of the *Journal of the Chemical Society* (London), died on January 31, 1921, in his fiftieth year. Throughout his scientific career, Dr. Cain was closely associated with the British dyestuff industry. During the war he served on Lord Moulton's staff, advising as to the convertibility of chemical factories for explosives manufacture. He later was in charge of H. M. Factory, Hackney Wick, and still later was transferred to the Technical Committee of British Dyestuffs, Ltd. Dr. Cain was the author of "The Synthetic Dyestuffs and Intermediate Products," "Chemistry of the Diazo Compounds," and "The Manufacture of Intermediate Products for Dyes." His revision of Roscoe and Schorlemmer's "Non-Metallic Elements" appeared only a short time before his death.

Dr. J. D. Pennock, general manager of the Solvay Process Co., died on March 11, at Syracuse, N. Y.

Dr. Ernst J. Lederle, who was health commissioner of New York City during two administrations, that of 1902 to 1904 and from 1910 to 1914, died at Goshen, N. Y., March 7. Dr. Lederle was one of the few health commissioners of New York who was not a physician. He was born in Staten Island in 1865, and was graduated from the Columbia School of Mines in 1886, later receiving from the same university the degrees of Ph.D. and Sc.D. He founded the Lederle Laboratories and the Lederle Antitoxin Laboratories, which are now merged with the firm of Lederle and Provost.

Mr. Jacob Hasslacher, well known in chemical circles, and until a year ago an active member of the firm of Roessler & Hasslacher Chemical Co., which he helped to establish in 1889, died at his home in New York City on March 15, 1921, at the age of 69. Mr. Hasslacher was born in Ems on-the-Lahn, Germany, and became a naturalized citizen of the United States in 1899. He was the leading factor in the formation and subsequent development of the Niagara Electro Chemical Company and the Perth Amboy Chemical Works, as well as other enterprises in which the company is interested.

Dr. John Iredelle Dillard Hinds died at Nashville, Tenn., March 4, 1921, at the age of 74 years. Dr. Hinds was for over 40 years a professor of chemistry in Cumberland University, the University of Nashville, and Peabody College, and at the time of his death was chemist of the Tennessee Geological Survey.

Dr. William F. Jones, a chemist who was prominent in the development of the pyroxylin industry, died recently at his home at Colonial Heights, Tuckahoe. Dr. Jones was born in Hillsboro, N. C., and was educated at Wake Forest College and Johns Hopkins University.

Dr. F. P. Dewey, chief chemist of the Mint Bureau of the U. S. Treasury, Washington, D. C., died February 12, 1921.

Mr. Hyman Bornstein has entered the employ of Deere & Co., Moline, Ill., as metallurgical engineer, where his duties will be in connection with metallurgical problems in the manufacture of agricultural implements. Mr. Bornstein's previous position was chemical engineer of the Bureau of Engineering, City of Chicago, Ill.

Mr. Philip Drinker has left the Buffalo Foundry and Machine Co., Buffalo, N. Y., where he was employed in the sales engineering department, and is now engaged in research work in the laboratory of applied physiology at the Harvard Medical School, Boston, Mass.

Mr. Ralph W. Boyd has resigned as chemist of the metallurgical research department of the Colorado School of Mines, and has become associated with the Desert Shale Oil Corporation of Salt Lake City.

Mr. M. A. Hurtt, formerly connected with the By-Product Coke Works of the Illinois Steel Co., Gary, Indiana, has become general foreman of the By-Product Coke Works of the Pittsburgh Crucible Steel Co., Midland, Pa.

Mr. W. R. Holt, formerly with the chemical division of Procter & Gamble Co., is now plant superintendent with the Harris Soap Co., Buffalo, N. Y.

Mr. C. L. Voress, who was in charge of the experimental and development work of the "Charcoal Absorption Process" at the plants of the United Natural Gas Co., and the B. B. Stroud Co., at Bradford, Pa., has been made general manager of the newly incorporated Gasoline Recovery Corporation, New York, and Mr. Vernon C. Canter, formerly with Procter & Gamble Co., and more recently with Mr. Voress, has been given active charge of all the experimental and development work at Bradford, Pa.

Mr. Wilson H. Low resigned as head chemist of the Cudahy Packing Company last June, after 22 years of service in that capacity, and has entered partnership with his former head assistant, Mr. John H. Show, in Los Angeles, Cal.

Mr. P. B. Place, a recent graduate of New Hampshire College, is at present employed as junior chemist at the U. S. Bureau of Mines, Pittsburgh, Pa.

Mr. Alfred N. Finn, formerly in the research department of the Hydraulic Steel Co., Cleveland, Ohio, has been reinstated as associate chemist at the Bureau of Standards, Washington, D. C., where, previous to the past year, he had been engaged for about nine years in the chemical testing of structural materials and miscellaneous supplies. His present assignment is in chemical control of the manufacture of optical glass.

Mr. H. J. Nimitz resigned as manager of the feed department of the Buckeye Cereal Co., Massillon, Ohio, in order to become superintendent of the feed department and chemist with the Brooks Milling Co., Minneapolis, Minn.

Dr. Lula Gaines Winston has resigned as head of the department of chemistry at the State Normal School for Women, Farmville, Va., and holds a similar appointment at Meredith College, Raleigh, N. C.

Mr. G. E. Webster, who was discharged last November from the Ordnance Department where he last served as army inspector of ordnance, property responsibility officer, and in other capacities, was reinstated as chemist at Picatinny Arsenal in December 1920.

Mr. F. P. Monaghan, for the past ten years superintendent for the Burt Portland Cement Co., of Bellevue, Mich., is employed in a similar capacity with the Glens Falls Portland Cement Co., Glens Falls, N. Y.

Dr. Philip L. Blumenthal has left the Babcock Testing Laboratory of Lackawanna, N. Y., and is now with the Lactal Analytical Laboratories, Inc., Buffalo, N. Y.

Mr. Leicester Patton resigned as chief of the Buffalo Station, Bureau of Chemistry, and has accepted a position with the Brocton Fruit Products Co., Brocton, N. Y., as chemist and production manager.

Mr. Julius Gorzo has changed from his former business of chemical engineering, and is now with the Pittsburgh Industrial Engineering Service, Pittsburgh, Pa., where he takes charge of the engineering and sales departments.

Mr. Armin R. Brandt has resigned as chief chemist for the Amazon Rubber Co., Akron, O., and is now acting in a similar capacity for the Isleworth Rubber Co., Ltd., Isleworth, England.

Dr. A. L. Kibler has accepted the transfer from Picatinny Arsenal, where he served as chief chemist, to the Old Hickory Powder Plant, Jacksonvill, Tenn., for the purpose of supervising the recovery of platinum from contact mass owned by the Ordnance Department.

Mr. H. W. Blanchard recently severed his relations with the chemical division of Procter & Gamble Co., Cincinnati, O., and at present is connected with the physics department of Purdue University, LaFayette, Ind.

Mr. M. E. Campbell has left the United British Refineries of Trinidad, B. W. I., and has accepted the position of chief chemist for the Continental Mexican Petroleum Co., Tampico, Tamaulipas, Mexico.

An Industrial Fellowship has been established at the University of Pittsburgh by Mrs. Fredonia J. Pratt, of St. Louis, Mo., as a memorial to her husband, the late Dr. David S. Pratt, former assistant director of the Mellon Institute, for research in that field of organic chemistry in which Dr. Pratt was especially interested.

Mr. R. L. Sibley, formerly employed as research chemist by the Goodyear Tire & Rubber Co., Akron, O., is now connected with the Intelligence Section of the Development Department of the Standard Oil Company of New Jersey.

Mr. Allen E. Stearn, formerly assistant professor of chemistry in the University of West Virginia, Morgantown, W. Va., has accepted a similar position in the University of Missouri, Columbia, Mo., where he has charge of the work in electro- and physical chemistry.

Mr. Martin S. Kissel, formerly of Brooklyn, N. Y., is now connected with the Sun Cheong Milling Co. of Shanghai, China, in the capacity of chief chemist.

GOVERNMENT PUBLICATIONS

By NELLIE A. PARKINSON, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Opium. Exportation of opium, hearings before subcommittee on H. R. 14500, to amend Section 6 of the act approved January 17, 1914 (to amend) the act to prohibit the importation and use of opium for other than medicinal purposes, approved February 9, 1909; January 3 and 4, 1921. Part 2. 168 pp. 1921.

Opium. Exportation of opium, hearings on S. 4553, to amend Section 6 of the act approved January 17, 1914 (to amend) the act to prohibit the importation and use of opium for other than medicinal purposes, approved February 9, 1909; December 11, 1920. 25 pp.

Containers. Food and drug containers, hearing on H. R. 10311, further to amend Section 8 of the act for preventing the manufacture, sale, or transportation of adulterated or misbranded or poisonous or deleterious foods, drugs, medicines, and liquors, and for regulating traffic therein, approved June 30, 1906, and amended by the act approved March 3, 1913. 30 pp. 1921.

Eggs. Frozen eggs, hearings before Committees on Agriculture and Forestry on H. R. 9521, to prevent hoarding and deterioration of, and deception with respect to, cold storage foods, to regulate shipments of cold storage foods in interstate commerce, and for other purposes. 40 pp. 1921. These hearings were held at a joint meeting of the Senate Committee on Agriculture and Forestry and the House Committee on Agriculture.

Nitrogen. Sundry civil appropriation bill (fiscal year, 1922), nitrate plant at Muscle Shoals, hearing before subcommittee on H. R. 15422. 28 pp. 1921.

TARIFF COMMISSION

Dyes and Dyeing. Census of dyes and coal-tar chemicals, 1919. Tariff Information Series 22. 95 pp. Paper, 20 cents. 1921.

BUREAU OF INTERNAL REVENUE

Alcohol, Denatured. Supplement to Regulations 60 relative to dealing in, transportation, and use of tax-paid industrial alcohol in original stamped packages only. Treasury Decision 3106. From Treasury Decisions 38, No. 51-53. 6 pp. 1921.

WAR DEPARTMENT

Lubricating Oils, Specifications and Method for Testing. Air Service Information Circular, Heavier-than-Air, 2, No. 118, October 20, 1920. 7 pp.

INTERIOR DEPARTMENT

Petroleum. Operating regulations to govern the production of oil and gas, under the act of February 25, 1920. Public Document 146. 4 pp. 1921.

INDIAN AFFAIRS OFFICE

Mineral Lands. Regulations (approved November 12 and December 27, 1920) governing leasing for lead and zinc mining operations and purposes, of restricted Indian lands in Quapaw Agency, Oklahoma, under the acts approved June 7, 1897, and March 3, 1909. 21 pp. 1921.

GEOLOGICAL SURVEY

Oil Possibilities in and around Baxter Basin, in the Rock Springs Uplift, Sweetwater County, Wyoming. A. R. SCHULTZ. Bulletin 702. 107 pp. This preliminary report was prepared in order to make public certain data bearing on the presence of oil in Baxter Basin, in the Rock Springs uplift, in Wyoming, and on the occurrence of oil shale around the uplift. A brief summary is given of the occurrence of oil shale in the late ter-

tiary beds around the greater part of the Rock Springs uplift, as well as the review of some facts which indicate that the central area of the Rock Springs uplift probably contains oil and gas.

Geography, Geology, and Mineral Resources of the Fort Hall Indian Reservation, Idaho. G. R. MANSFIELD. With a chapter on Water Resources by W. B. HERBY. Bulletin 713. 152 pp. Paper, 50 cents. Under mineral resources the phosphate and metalliferous deposits, coal prospects, volcanic ash, and the soil composition are described.

The Future of Alaska Mining and the Alaskan Mining Industry in 1919. Papers by A. H. BROOKS AND G. C. MARTIN. Bulletin 714-A. Mineral Resources of Alaska, 1919-A. 103 pp. This is the sixteenth of a series of annual bulletins treating of the mining industry of Alaska and summarizing the results achieved during the year in the investigation of the mineral resources of the Territory. The report includes the more important economic results of the year. It contains an account of the mining industry, including statistics of mineral production and also preliminary statements on investigations made by the Geological Survey.

Potash Resources of Nebraska. W. B. HICKS. Bulletin 715-I. Contributions to Economic Geology. 1920. Part I. 15 pp. Published February 8, 1921. There are more than 100 known productive lakes in Nebraska, scattered over an area of some 800 sq. mi., and covering an aggregate area of more than 6097 acres. A summary of their estimated potash content is contained in the following table:

COUNTY	—Area (Acres)—		Brine Short Tons	Solids (Short Tons)—		Potash (K ₂ O) Short Tons
	Surface	Sub-surface		Surface	Sub-surface	
Sheridan.....	3,107	697	15,872,000	146,590	329,215	115,360
Garden.....	1,147	196	4,655,000	103,150	83,440	40,910
Morrill.....	502	130	2,607,700	40,880	42,020	17,670
Box, Butte, and Cherry.....	150	38	266,000	750	13,720	2,440
In doubt.....	1,191	263	9,353,000	76,260	105,190	38,730
TOTAL.....	6,097	1,324	32,753,700	367,655	573,585	215,110

Phosphate Rock near Maxville, Granite County, Montana. J. T. PARDEE. Bulletin 715-J. Separate from Contributions to Economic Geology. 1920. Part I. 5 pp. Published February 7, 1921. The quantity of minable material in these deposits is at least as great as that in the known deposits near Melrose, Garrison, and Elliston, and they are less than 6 miles from the railway.

The Divide Silver District, Nevada. ADOLPH KNOPF. Bulletin 715-K. Contributions to Economic Geology. 1920. Part I. 28 pp. Published February 12, 1921. The discovery of silver ore that started the great activity at this camp was made late in 1917, wholly by chance. The chief producing mine is the Tonopah Divide, which yields ore averaging 25 ounces of silver and \$2.50 in gold to the ton.

The Mogollon District, New Mexico. H. G. FERGUSON. Bulletin 715-L. Contributions to Economic Geology. 1920. Part I. 34 pp. Published February 8, 1921. The ores of the district are valuable mainly for silver. Argentite, pyrite, bornite, chalcocopyrite, and tetrahedrite, together with small amounts of horn silver and native silver, are the principal ore minerals. The ores are principally sulfides.

Coal in the Middle and Eastern Parts of San Juan County, New Mexico. C. M. BAUER AND J. B. REESIDE, JR. Bulletin 716-G. Contributions to Economic Geology. 1920. Part II. 83 pp. Published February 11, 1921. The coal is chiefly of subbituminous rank, but in the northern part of the field it is good enough to be ranked as bituminous. The beds, numbering from two to six at most localities, range in thickness from a few inches to 40 ft. The thickness of the various beds at many places is given, and the quality and character of the coal and the inclosing strata are described.

Character of Coal in the Thomas Bed near Harrison, West Virginia. M. R. CAMPBELL. Bulletin 716-H. Contributions to Economic Geology. 1920. Part II. 3 pp. Published February 18, 1921. Chemical analyses show that this coal is a semibituminous or smokeless coal, which is rather high in ash and contains a variable amount of sulfur.

Coal in 1918. Part B. Distribution and Consumption. C. E. LESHER. Separate from Mineral Resources of the United States. 1918. Part II. 78 pp. The statistics collected from

the operators of coal mines and published in this report show the quantities of bituminous coal and lignite (1) used at the mines for generating steam and heat, (2) sold locally or used by employees, (3) used at the mines for making coke (none of this coal is shipped), and (4) shipped to market either by rail or by river.

Chromite in 1919. J. S. DILLER. Separate from Mineral Resources of the United States. 1919. Part I. 5 pp. Published February 4, 1921. The total domestic chromite of all grades shipped from mines in 1919 amounted to 5079 long tons, valued at \$129,302, or \$25.46 a ton, a decrease of nearly 94 per cent in quantity and nearly 97 per cent in value from the shipments of 1918, although it exceeded the domestic output during any year before the war.

Secondary Metals in 1919. J. P. DUNLOP. Separate from Mineral Resources of the United States. 1919. Part I. 35 pp. Published January 31, 1921. The following tabular statement shows the secondary metals of certain classes recovered in the United States in 1918 and 1919:

	1918		1919	
	Quantity Short Tons	Value	Quantity Short Tons	Value
Copper, including that in alloys other than brass.....	122,510	\$ 60,519,900	112,400	\$41,812,800
Brass scrap remelted..	328,800	128,696,300	249,700	75,944,100
Lead as metal.....	41,146	13,788,200	{ 55,684	12,942,600
Lead in alloys.....	55,954		{ 66,416	
Zinc as metal.....	27,108	6,950,600	{ 39,910	6,711,900
Zinc in alloys other than brass and in chemical compounds	11,082		{ 6,062	
Tin as metal.....	7,142	41,381,000	{ 5,977	29,868,200
Tin in alloys.....	16,695		{ 18,056	
Antimony as metal....	43	1,317,000	{ 48	717,900
Antimony in alloys....	5,183		{ 4,351	
Aluminum as metal....	6,050	10,113,600	{ 6,017	12,014,600
Aluminum in alloys....	9,000		{ 12,674	
Nickel as metal.....	178	1,532,300	{ 163	1,829,400
Nickel in nonferrous alloys.....	1,215		{ 2,284	
TOTAL.....		\$264,298,900		\$181,841,500

Mineral Waters in 1919. A. J. ELLIS. Separate from Mineral Resources of the United States. 1919. Part II. 35 pp. Published January 21, 1921. The statistics in this report refer only to domestic mineral waters that have been sold, imports being excepted. Three uses of mineral waters are recognized—table use, medicinal use, and use in the manufacture of soft drinks. The reports show that as many as 81 waters are sold in the United States for both table and medicinal purposes, and that 22 waters are sold for table use, medicinal use, and use in the manufacture of soft drinks.

BUREAU OF MINES

Use of the MacMichael Viscosimeter in Testing Petroleum Products. W. H. HERSCHL (Bureau of Standards) AND E. W. DEAN. Reports of Investigations. Serial No. 2201. 12 pp. Issued January 1921. The aim of the paper is to outline in a simple manner the principles involved in the calibration and use of the MacMichael viscosimeter and to describe a procedure that has proved satisfactory in the respective laboratories of the authors.

Properties of Typical Crude Oils from the Eastern Producing Fields of the United States. E. W. DEAN. Reports of Investigations. Serial No. 2202. 57 pp. Issued January 1921. Results of the laboratory analysis of 35 samples of crude petroleum representing the so-called Eastern fields are offered for purposes of general information. Figures for a few samples from Mid-Continent and the Western States are included for the purposes of comparison. Attention is called to several conclusions of general significance. Figures for approximate refining yields are given for purposes of rough and ready comparison.

Consumption of Reagents Used in Flotation. THOMAS VARLEY. Reports of Investigations. Serial No. 2203. 4 pp.

The Talc Industry in 1920. R. B. LADOO. Reports of Investigations. Serial No. 2204. 5 pp. Issued January 1921. The production of talc in 1920 was probably the largest in history, and imports of talc were larger than ever before.

Investigation of Low-Grade and Complex Ores in Colorado. R. R. HORNOR AND W. H. COGHILL. Reports of Investigations. Serial No. 2206. 4 pp.

Tests of Carbon Monoxide Detector in Mines. D. HARRINGTON AND B. W. DYER. Reports of Investigations. Serial No. 2207. 3 pp. Issued January 1921.

The Value of Oxygen Breathing Apparatus in Mine Rescue Operations. D. J. PARKER. Reports of Investigations. Serial No. 2209. Issued January 1921. 3 pp.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. BURROUGHS. Reports of Investigations. Serial No. 2210. 25 pp. Issued January 1921.

BUREAU OF STANDARDS

Annual Report of the Director of the Bureau of Standards to the Secretary of Commerce for the Fiscal Year Ended June 30, 1920. Miscellaneous Publications—No. 44. 281 pp. 1920.

Lime—Definitions and Specifications. Circular 106. 15 pp. Paper, 5 cents.

DEPARTMENT OF AGRICULTURE

Nicotine Sulfate in a Dust Carrier against Truck-Crop Insects. R. E. CAMPBELL. Department Circular 154. 15 pp. Paper, 5 cents. Issued February 21, 1921.

Articles from Journal of Agricultural Research

Degree of Temperature to Which Soils Can Be Cooled without Freezing. GEORGE BUOYOCOS. 20 (November 15, 1920), 267-9.

Changes Taking Place in the Tempering of Wheat. E. L. TAGUE. 20 (November 15, 1920), 271-5.

Carbon Dioxide Content of Barn Air. M. F. HENDRY AND ALICE JOHNSON. 20 (December 15, 1920), 405-8.

Daubentonia Longifolia (Coffee Bean), a Poisonous Plant. C. W. MARSH AND A. B. CLAWSON. 20 (December 15, 1920), 507-13.

Nodule Bacteria of Leguminous Plants. F. LÖHNIS AND ROY HANSEN. 20 (January 3, 1921), 543-55.

Measurement of the Amount of Water That Seeds Cause to Become Unfree and Their Water-Soluble Material. G. J. BOUYOCOS AND M. M. MCCOOL. 20 (January 3, 1921), 587-93.

Concentration of Potassium in Orthoclase Solutions Not a Measure of Its Availability to Wheat Seedlings. J. F. BREAZEALE AND L. J. BRIGGS. 20 (January 15, 1921), 615-21.

Composition of Tubers, Skins, and Sprouts of Three Varieties of Potatoes. F. C. COOK. 20 (January 15, 1921), 623-35.

Further Studies in the Deterioration of Sugars in Storage. NICHOLAS KOPELOFF, H. Z. E. PERKINS AND C. J. WELCOME. 20 (January 15, 1921), 637-53.

Effect of Various Crops upon the Water Extract of a Typical Silty Clay Loam Soil. G. R. STEWART AND J. C. MARTIN. 20 (January 15, 1921), 663-67.

COMMERCE REPORTS—FEBRUARY 1921

The leather situation in Bulgaria is reviewed. (Pp. 609-10)

The production of olive oil in Greece is described and statistics showing the production by districts. (Pp. 665-6)

Serious consideration is being given to the use of fuel oil in place of coal in Italy. (Pp. 668-9)

Recent experiments indicate that indigo grown in Assam will prove a formidable competitor of synthetic indigo. A very large share of Indian indigo has been grown in the Province of Bihar, but the exhaustion of the fertility of the soil has caused a great decrease in the yield. It is believed that this situation should open up a market for American fertilizers. (P. 684)

The following table shows the production (in kilos) of metals and minerals in Mexico for the years 1917 to 1920; the figures for 1920 being of a preliminary nature subject to later rectification:

	1917	1918	1919	1920
Gold.....	23,542	25,313	23,586	23,370
Silver.....	1,306,988	1,944,542	2,049,898	1,979,972
Copper.....	50,985,923	70,223,455	56,172,235	46,056,900
Lead.....	64,124,752	98,837,154	71,375,968	121,434,066
Zinc.....	45,180,778	20,698,996	11,559,685	14,363,057
Mercury.....	33,132	163,597	118,940	77,228
Antimony.....	2,646,544	3,278,546	470,738	1,572,376
Graphite.....	420,046	6,190,849	4,023,015	2,991,529
Tungsten.....	187,637	149,486	21,970	34,917
Tin.....	9,214	13,538	1,588
Arsenic.....	1,284,820	1,881,011	2,246,378	1,198,806
Manganese.....	73,357	2,878,383	2,294,227	838,624
Molybdenum.....	27,371	1,767	648

(P. 709)

The Czechoslovak hide and leather industry is reviewed. (P. 718)

Business conditions were so unfavorable during 1920 that no new graphite-producing districts were opened in Madagascar, no new company for its exploitation was formed, and operations at a number of the old deposits ceased. (P. 720)

Statistics of Siam's imports of chemicals and drugs show the substantial progress made by the United States in this trade during the last seven years. (P. 733)

By a decree dated December 10, 1920, sesquisulfide of phosphorus is included in the section "raw materials" for use in industry, when imported into Uruguay, with a valuation of 1.50 pesos per kilo and a duty of 8 per cent of this valuation. (P. 751)

In normal years India produces well over 5,000,000 tons of oil seeds, one-third of which is usually exported. These seeds include cottonseed, rape seed, peanuts, sesame seed, mowra seed, poppy seed, linseed, castor seed, as well as copra. (P. 772-3)

The fluospar industry is reported to be active in Germany. Most of the fluospar is consumed at present by the German iron industry. (P. 788)

A diminished production in the Norwegian paper industry is reported. (P. 809)

The production, transportation, storage, composition, specifications, uses, prices, and exports of wood oil in China are described. (Pp. 812-5)

The Italian restriction on the importation of crude and refined mineral oil has been removed. (P. 833)

A reward has been offered in New South Wales to the first producer of 100,000 gallons of petroleum within the State. (P. 840)

An industry for the supply of toilet preparations made from talc, graphite, black oxide, many different water colors, manganese, tailors' chalk, colored ochres, healing ointment, etc., has been started in Tasmania, and a company floated to produce all of these articles from the raw material. (P. 840)

Picked samples from Manitoba's new nickel-copper and gold camp have shown values of 10 per cent in nickel and 20 per cent in copper, with considerable gold. (P. 848)

Mineral production in Canada during 1920 is estimated at \$200,000,000, compared with \$176,686,390 in 1919. (P. 848)

An Italian company has developed a process for obtaining mineral oil with an exceedingly low bituminous content from Sicilian asphalt. (P. 852)

Statistics are given showing the imports and exports of vegetable oils and vegetable oil material by Sweden during the years 1917, 1918, and 1919. (Pp. 854-5)

The Estonian Ministry of Trade and Industry has established factories for drying potatoes and making potato flour along the lines employed by Germany during the war. (P. 855)

Poland has been negotiating with the Chilean government for the purchase of 300,000 tons of nitrate a year on a credit guaranteed by the Chilean government. If this arrangement is effected, a large part of the present surplus stocks will be disposed of. (P. 857)

Statistics are given showing the imports and exports of vegetable oils and vegetable oil material by French India during the years 1912, 1913, and 1914. (P. 861)

After thorough investigation it is stated that flavoring extracts and coloring matter are the only articles which can be profitably sold to the Argentine candy manufacturers by the American exporter. (P. 872)

The production and marketing of olives and olive oil in Greece are described. (Pp. 874-5)

Advice from Alexandria, Egypt, states that there can be but a very limited market for industrial chemicals with the exception of fertilizers, brewery supplies, etc. There is, however, a good market for drugs and certain of the lighter chemicals. (P. 888)

In view of the almost total lack of potash fertilizers, the agriculturists of Piedmont, Italy, are urging that the Ministry of Finance in Rome turn over to a private concern the utilization of the salt fields from which an enormous quantity of fertilizers could be obtained. (P. 895)

Potassium salts have been recently discovered in nearly all of the numerous salt wells in Szechwan Province, which range in depth from 1000 to 3000 ft. The mother liquor contains about 3.5 per cent of potassium. (P. 896)

Statistics are given showing the imports and exports of vegetable oils and vegetable oil material by the French Oceania during the years 1912, 1913, and 1914. (Pp. 918-9)

A scarcity of soda in Czechoslovakia is reported and it is stated that the amount available will supply only about 30 per cent of the needs of the glass factories and other concerns using that product. (P. 934)

The Czechoslovak iron industry is reported to be suffering from the competition of German iron producers. (Pp. 934-5)

A decrease is shown in the imports of chemicals and drugs into Madras, India, for the year ending March 31, 1920, but a continued expansion in the imports of dyes and colors was quite notable. (P. 950)

The Warsaw Agricultural Syndicate has a plan whereby farm products are to be exchanged for fertilizers in Poland. (Pp. 957-9)

Statistics are given showing the trend of prices in the German leather industry. (P. 967)

Statistics are given showing the production of rubber on plantations in the Dutch East Indies during the years 1918, 1919, and 1920. This production has shown a large and steady annual increase since 1913. (P. 971)

The British Board of Trade has prohibited the exportation of ammonium sulfate, superphosphate, lime, basic slag, and compound fertilizers containing any of these products. (P. 977)

A concern in Jaffa, Palestine, writes that it can export Arabic gum and myrrh, and would like to get in touch with American firms manufacturing these substances. (P. 1040)

There has been a steady reduction in the output of petroleum in Japan since 1915, but experts believe that there will be a gradual increase, beginning this year. (Pp. 1044-5)

The prices of all French industrial metals dropped in 1920 because of the holding off of buyers, and prices to-day are about equal to those at the lowest point in 1915. (P. 1045)

Unfavorable conditions are reported in the Malayan rubber industry. (Pp. 1064-5)

A revised list of the importers and dealers in chemicals and drugs in China, giving available information as to their relative number, nationality, and whether wholesale or retail, is now available at the Bureau of Foreign and Domestic Commerce. (P. 1100)

Tests extending over several months have passed the experimental stage and conclusively demonstrate that peat, reduced to powder or prepared in the form of briquets, makes an excellent substitute for coal as fuel for locomotives on Swedish railways. (P. 1109)

Statistics are given showing the imports and exports of vegetable oils and vegetable oil material by Federated Malay States—Parak, Selangor, Negri Sembilan, and Pahang—during the two years for which statistics are available. (P. 1131)

Specifications for aviation petrol from Roma oil bore points, Queensland, are much more stringent regarding the content of the constituents for higher boiling point than those for ordinary motor fuel. With regard to the absence of higher boiling-point fractions the petrol is well within the limits prescribed by the United States Fuel Administration for aviation petrol, domestic grade, though as regards volatility the petrol is not quite up to specifications. (P. 1132)

The production of zinc in Japan in 1915 reached 21,131 tons, which was sufficient to cover the local demand. Consumption steadily increased until the height of production was reached in 1917. Since then the demand has gradually decreased, and at present only three factories that use materials produced in their own mines are continuing business. (P. 1156)

SPECIAL SUPPLEMENTS ISSUED RUSSIA—16c

STATISTICS OF EXPORTS TO THE UNITED STATES		
JAPAN—(P. 663)	BAHAI—(P. 823, 889)	ITALY—(P. 915)
Menthol crystal	Castor beans	Citrate of lime
Peppermint oil	Hides and skins	
	Chrome ore	MADRAS—(Pp. 956-7)
SYDNEY, NOVA SCOTIA—(P. 671)	Manganese ore	Copra
Pulpwood	Oils:	Indigo
Creosote oil	Vegetable—castor, crude	Monazite sand
Sulfate of ammonia	Rubber	Nux vomica
	Medicinal roots and leaves	Oils:
CHINA—(P. 727)	Carnauba wax	Coconut
Sesame seed		Lemon grass
Sesame oil		Sandalwood
		Ore, chrome
EGYPT—(P. 749)	FRANCE—(Pp. 898, 997)	Rubber
Colocynth	Drugs, crude	Turmeric
Gum arabic	Ammonium nitrate	
Senna	Chalk, crude	LONDON—(P. 1041)
Oil, fuel	Chicory root	Leather
	Chemical products	Hides
	Raw hides	Tin
NAPLES, ITALY—(P. 771)		Gums
Tartar	MARSEILLE, FRANCE—(P. 975)	Drugs and chemicals
	Chemicals	Aluminium
BRITISH GUIANA—(P. 856)	Drugs	Linseed oil
Bauxite	Dyes	
	Olive oil	GREECE—(P. 665)
		Ripe olives

BOOK REVIEWS

The Chemistry of Enzyme Actions. By K. GEORGE FALK. [American Chemical Society Monograph Series.] 136 pages. The Chemical Catalog Co., Inc., New York, 1920. Price, \$2.50.

This monograph is the first of two series to be published under the auspices of the AMERICAN CHEMICAL SOCIETY. According to the statement of the committee in charge of their preparation and publication, these monographs are to serve a dual purpose. The first purpose, which must be of vital interest to every member of the SOCIETY, is to present the knowledge available upon the subject in a readable form, intelligible to those whose activities may be along wholly different lines. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended, together with extended references to the literature, or at least a critical selection of the most important papers dealing with the subject at hand.

In the introductory chapter the general problem of enzymes and enzyme action is outlined. Two lines of investigation are suggested: the one a study of the kinetics of enzyme action, the other the study of enzymes as chemical substances possessing definite chemical structures or configurations. These two thoughts predominate in the discussions in Chapters I and II, and in Chapter III, where the subject of catalysis is taken up. Enzymes are catalysts; they are not used up, neither are they destroyed, but by their mere presence set in motion a reaction between two other substances. Since the chemical reactions whose velocities are increased by enzymes include a number of comparatively simple reactions (as well as many complex ones) and can be brought about also by simple chemical means, though very much more slowly, these simple chemical changes are discussed in Chapter IV. The enzyme which accelerates the reaction is neglected and attention is directed to the reaction itself. The hydrolysis of sucrose by acid is discussed and the amount of change produced is studied by:

- (a) The rotation of the plane of polarized light.
- (b) The change in viscosity.
- (c) The reducing power of the hexoses formed upon alkaline cupric salt solutions such as Fehling's solution and others.

The three sets of theories to account for catalytic action of acids on the hydrolysis of sucrose are mentioned. First, the reaction is considered as due entirely to hydrogen ions present in solution; second, the dual theory assumes the action to be due both to the hydrogen ions and to the un-ionized molecules; third, the addition theory of chemical reactions assumes a primary formation of an addition compound with the acid molecule and considers that the solvent is involved as one of the main factors, while the ionization is secondary. None of these three views has been found completely satisfactory, but the writer suggests a preference to the last mentioned. Oxidizing and reducing enzymes appear even more difficult to handle from the theoretical side than do the hydrolytic reactions due to enzyme activity.

Chapter V considers the physical properties common to enzyme preparations. Their colloidal character and non-dialyzability through collodion membranes, their absorption by other colloids, their precipitation or coagulation either by the addition of a foreign substance to the solution, or by the removal from the solution of a substance apparently essential in holding the enzyme in solution are discussed. Mention is also made of the importance of the reaction of the medium to

the activity of the enzyme, and tabulated data are given of the recognized optimum hydrogen-ion concentration necessary for best activity.

In Chapter VI the chemical properties common to all enzyme preparations are considered. Every such preparation which has been examined contains nitrogen, and a table is given showing the nitrogen content of some of these preparations. The inorganic elements, as well as carbon and hydrogen, are too difficult to treat with our present knowledge. Attention is called to the fact that no enzyme has actually been isolated and their chemical formulas are still a matter of conjecture. Interesting parallels between the behavior of indicators and of enzymes are pointed out. The interrelation in enzymatic activity between the three factors: temperature, hydrogen-ion concentration, and time, is shown, as well as the fact that the optimum pH value for the enzyme may vary for the different substrate being acted upon. Finally, the activating and inhibiting actions of certain inorganic substances are considered.

Chapter VII considers the mechanism of enzyme actions and deals with the velocities of the chemical reactions, the factors which influence them and the inferences which may be drawn concerning the enzyme actions involved.

In the next chapter the author discusses the uses and applications of enzymes. Here, the chemist whose activities are along an entirely different line gets his first introduction to what the previous eight chapters are all about. It is shown that the enzymes are catalysts produced by living animal and vegetable matter, the function of which is to break down and render assimilable food for growth and renewal of tissues or their component cells. The actions of enzymes therefore consist in favoring or accelerating those reactions which are required in the life process and making possible its continuance.

The uses of enzymes are roughly divided into five groups:

- Industrial application of enzymes
- Enzymes of metabolism and catabolism
- Enzymes in plant growth
- Bacterial enzymes
- Enzymes in laboratory work

This list does not tend to be complete. In the industrial application mention is made of the fermentation industry, the production of glycerol, of acetone, succinic acid, acetic acid, formic acid, fusel oils, and esters. It is also suggested that a new thought may be possible, *viz.*, the synthesis of complex molecules out of simpler ones, in contrast to the cleavage of complex ones as practiced to-day.

There is a typographical error in the table on page 121, where melibiose instead of melibiase is shown to hydrolyze melibiose into galactose and glucose. The term sucrase in the same table is obsolete, invertase being the name at present used for this enzyme, and also that used by Hudson in the article mentioned.

In Chapter X the author sums up what has appeared in the previous chapters, adding a discussion of the specificity of the enzymes. An enzyme which acts upon starch cannot act upon protein or fat, and vice versa.

Co-enzymes are taken up. Reference is made to the activation of the pancreatic lipase by the bile salts and to the activation of pancreatic amylase by salt, etc., and the suggestion is made that the word co-enzyme be dropped from the literature and that an attempt be made to study the problem of activation from a purely chemical standpoint.

In commenting upon this monograph, the first thing that seems lacking is an extended bibliography. The references.

given are all too few, and they would have been much more serviceable had they been properly classified at the end of the book. On the whole, the book is well written and shows much painstaking effort on the part of the author. For the specialist and research worker in this and allied lines, this book will prove of inestimable value, and it certainly deserves a place in the library of such men. I would point out, however, the need of pure enzymes for further research. If the studies of enzyme action are to be pursued, it is absolutely necessary that pure enzymes be made much purer than most at present at the disposal of the workers. Much of the conflicting evidence now recorded may undoubtedly be traced to variations in the purity of the enzymes under investigation. It is the reviewer's opinion that the author did not lay sufficient stress upon this fact.

For the chemist whose activities may be along a wholly different line, it is a question whether his interest could be held through the discussions in the first four chapters sufficiently for him to finish the book. Inasmuch as this is the first of the series, it is to be hoped that the monographs to follow have an extended bibliography in the back, properly indexed, and that as much attention be devoted to the subject to develop it from the practical as from the theoretical standpoint.

HOWARD T. GRABER

The Determination of Hydrogen Ions. By W. MANSFIELD CLARK. 318 pp. Williams and Wilkins Co., Baltimore, Md., 1920. Price, \$5.00.

The present volume is frankly written for the biologist and the biological chemist. Within the past decade we have awakened to the fact that "titratable acidity" is a relatively unimportant factor in living processes, while the actual H^+ -ion concentration is of paramount importance. Originating with the epoch-making researches of Sørensen, whose portrait very properly forms the frontispiece of this book, exact methods for the determination of hydrogen ions have been used more and more extensively by biological workers. Michaelis in 1914 published "Die Wasserstoffionenkonzentration" and gave a new impetus to the work. However, the apparatus which Sørensen and Michaelis used appears very complicated and formidable to those who have not been trained in the niceties of physical chemistry, with the result that no doubt many workers have decided that they were not sufficiently skilled to undertake H^+ -ion work. Such a fear need no longer be felt. The reviewer is proud of the enormous advances that American manufacturers have made in designing apparatus for the exact determination of hydrogen ions, making the process so simple that anyone can master it within a very few hours.

In America we have had this advantage of fine apparatus for several years, but have of necessity been forced to depend for guidance on Michaelis' book and on a great mass of data scattered through many scientific journals. Now we have this admirable work by Dr. Clark in which we can find a ready answer to most of our perplexing questions.

The first seven chapters of the book are devoted to the colorimetric methods of H^+ -ion determination. Surely no one could write more convincingly in this field than the author, for it is to him and his co-workers that we owe much of our present knowledge, and are indebted for a series of new, sensitive, and brilliant indicators.

Chapter I considers the general relations between acids and bases, dealing primarily with dissociation constants and neutralization curves. The author strongly emphasizes that we must distinguish sharply between what "we call 'normality' in its older sense, the *quantity* factor of 'acidity' and the hydrogen-ion concentration, the *intensity* factor." The outline of the colorimetric method includes an excellent color chart by means

of which H^+ -ion concentrations ranging from pH 1.2 to 9.8 may be roughly estimated. In discussing the theory of indicators, the author rightly points out that there are still many unknown factors in this field and that "there seems to be no inherent reason why ionization, tautomerism, alteration in the fields of force within the compound and light absorption should not (all) be correlated." Under "optical aspects" he considers among other questions those involving the psychology of the eye, pointing out that in dealing with a dichromatic indicator (blue and red) "the eye instinctively fixes upon the very dominant red." Further chapters deal with the choice of indicators, with standard buffer mixtures, and with the errors involved in colorimetric determinations, including the "protein error" and the "salt effect." Here the author frankly acknowledges that much additional research is needed before all of the factors can be known. He states:

We can bring to bear upon the problem no adequate explanation of the "salt effects," no general theory of the "protein errors," no comprehensive treatment of the optical difficulties, and finally no perfectly rigid basis upon which to compare the electrometric and colorimetric measurements. It seems wise to leave any detailed treatment of these subjects to painstaking research and to the resolution which will doubtless come when the conduct of strong electrolytes is placed upon a sound basis.

What a refreshing change from the all too common practice of stating one's pet hypothesis as actual fact! The colorimetric method is concluded in a chapter on approximate determinations with indicators.

The second part of the book deals with the electrometric method, and includes a discussion of the principles of the method, the theory of the hydrogen electrode, potential differences at liquid junctions, hydrogen and calomel electrodes and electrode vessels, the potentiometer, and hydrogen generators, wiring, etc. The discussion is full and to the point. The mathematical and physical formulas are presented concisely, but the text is handled in such a way that the formulas are a *help* to the understanding of the method, but not a *necessity*. Every detail of a successful electrometric installation is considered. In Chapter XIV the relation of hydrogen electrode potentials to reduction potentials is considered, and Chapter XV is devoted to sources of error in electrometric measurements of pH. For one who is just beginning electrometric measurements the advice found in this chapter alone will be invaluable. Chapter XVI is devoted to standard solutions for checking H^+ -ion measurements, and in Chapter XVII the author considers the question of the standardization of pH measurements. Everyone working with the potentiometric method should read this chapter, for the author points out that we still have no absolute unalterable standard, due to the various methods of effecting the liquid junction, the unknown temperature corrections, etc. He wisely suggests that the various workers should carefully state the exact conditions under which they carried out their measurements so that corrections, which we cannot now apply for lack of knowledge, may be applied in the future.

The last two chapters consider supplementary methods and the application of H^+ -ion methods in the various fields of activity. The book closes with a complete bibliographic citation of 1234 references, giving author (arranged alphabetically), year, title, and journal reference. An appendix containing several useful tables, as well as a list of equipment required for the electrometric method, closes the volume.

As stated above, the book was written for the biologist and the biological chemist. It should, however, be equally useful to everyone whose problems involve either *quantity* of acidity or *intensity* of acidity. Its place is not alone on the shelf of every chemical library, but on the working desk of every chemist whose problems involve the determination of hydrogen ions.

ROSS AIKEN GORTNER

NEW PUBLICATIONS

- Chemistry: Inorganic Chemistry for Schools and Colleges.** JAS. LEWIS HOWE. 2nd edition, revised. 3d edition of "Inorganic Chemistry According to the Periodic Law," by F. P. Venable and J. L. Howe. 443 pp. Price, \$4.00. The Chemical Publishing Company, Easton, Pa.
- Chemistry: Organic Chemistry for the Laboratory.** W. A. NOYES. 4th edition, revised. 293 pp. Illustrated. Price, \$3.50. The Chemical Publishing Company, Easton, Pa.
- Chemistry: Treatise on Chemistry.** H. E. ROSCOE AND C. SCHORLEMMER. Vol. I. The Non-Metallic Elements. Price, \$9.00. Vol. II. The Metals. Price, \$12.00. 5th edition, completely revised. 968 pp. Illustrated. The Macmillan Co., New York.
- Copper Refining.** LAWRENCE ADDICKS. 206 pp. Illustrated. Price, \$3.00. McGraw-Hill Book Co., Inc., New York.
- Dictionary of Chemical Solubilities—Inorganic.** ARTHUR M. COMEY AND DOROTHY A. HAHN. New edition, revised. Price, \$14.00. The Macmillan Co., New York.
- Elementary Dynamics: A Textbook for Engineers.** J. W. LANDON. 246 pp. Cambridge University Press, London.
- Oils: Lubricating and Allied Oils. A Handbook for Chemists, Engineers, and Students.** ELLIOTT A. EVANS. 128 pp. Price, 9s. 6d. (The Directly-Useful Technical Series.) Chapman & Hall, Ltd., London.
- Paper: The Manufacture of Pulp and Paper.** J. J. CLARK. Vol. I. Arithmetic, Elementary Applied Mathematics, How to Read Drawings, Elements of Physics. 441 pp. Illustrated. Price, \$5.00. McGraw-Hill Book Co., Inc., New York.
- Poisons: Laboratory Manual for the Detection of Poisons and Powerful Drugs.** WILHELM AUTENRIETH. Translated by WILLIAM H. WARREN. 5th American edition. 342 pp. Illustrated. Price, \$3.50. P. Blakiston's Son & Co., Philadelphia.
- Properties of Steam and Thermodynamic Theory of Turbines.** H. L. CALLENDAR. 531 pp. Price, \$14.00. Longmans, Green & Co., New York.
- Vitamines: Essential Food Factors.** BENJAMIN HARROW. 219 pp. Price, \$2.50. E. P. Dutton & Co., New York.
- ### RECENT JOURNAL ARTICLES
- Alcohol: Manufacture of Ethyl Alcohol from Wood Waste.** E. C. SHERARD. *Chemical Age*, Vol. 19 (1921), No. 2, pp. 76-79.
- Aluminium: Ferric Sulfate as a New Etching Reagent in the Metallography of Aluminium.** ROBERT J. ANDERSON. *The Metal Industry*, Vol. 19 (1921), No. 2, pp. 69-70.
- Atomic Structure: Atomi e Nuclei Atomici.** ROBERTO SALVADORI. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 1, pp. 13-19.
- Blast Furnace Gases: Electrostatic Precipitation Applied to Blast Furnace Gases.** H. J. BUSH. *The Chemical Age* (London), Vol. 4 (1921), No. 85, pp. 116-117.
- Calorizing as a Protection for Metals.** ARTHUR V. FARR. *The Iron Age*, Vol. 107 (1921), No. 4, pp. 251-254.
- Carbonization: Sulfur Distribution in Carbonization.** U. O. HUTTON AND C. C. THOMAS. *The Gas Age*, Vol. 47 (1921), No. 3, pp. 88-94.
- Charts: The Construction and Use of Alignment Charts.** A. J. V. UMANSKI. *The Chemical Trade Journal and Chemical Engineer*, Vol. 68 (1921), No. 1761, pp. 233-236; No. 1762, pp. 269-272.
- Chemical Engineering: Some Problems of Chemical Engineering.** A. R. WARNES. *The Chemical Trade Journal and Chemical Engineer*, Vol. 68 (1921), No. 1761, pp. 237-238; No. 1762, pp. 273-275.
- Chemical Industry: Theory and Practice in Chemical Industry, with Special Reference to Physical Chemistry.** E. B. R. PRIDEAUX. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 3, pp. 40-42.
- Chemical Methods of De-Aeration of Water or Solutions.** H. A. WHITE. *The Journal of the Chemical, Metallurgical and Mining Society of South Africa*, Vol. 21 (1920), No. 6, pp. 105-111.
- Clay: The "Why" of Aging Clay.** H. SPURRIER. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 2, pp. 113-118.
- Cobalt Brasses.** LEON GUILLET. *Chemical and Metallurgical Engineering*, Vol. 24 (1921), No. 10, pp. 439-443. Translated from *Revue de Metallurgie*, Vol. 17, No. 7, p. 494.
- Cottonseed Oil: On the Catalytic Hydrogenation of Cottonseed Oil.** LOUIS KAHLBERG AND GEORGE J. RITTER. *Journal of Physical Chemistry*, Vol. 25 (1921), No. 2, pp. 89-114.
- Direct Recovery Process for Flue Dust.** GEORGE B. CRAMP. *The Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 3, pp. 198-202.
- Dyes: Fastness Properties of the Principal Red Dyes.** BARRINGTON DE PUYSTER. *Color Trade Journal*, Vol. 8 (1921), No. 3, pp. 106-114.
- Dyes: Notes on the Manufacture of the Rhodamines.** RAFFAELE SANSONE. *Color Trade Journal*, Vol. 8 (1921), No. 3, pp. 84-88.
- Dyes: Sur la Coloration des Indigoids.** J. MARTINET. *Revue Generale des Matieres Colorantes de la Teinture, de l'Impression, et des Apprets*, Vol. 25 (1921), No. 290, pp. 17-18.
- Dyes: Standardization of Dyestuff Intermediates.** ERNEST FYLEMAN. *Journal of the Society of Dyers and Colourists*, Vol. 37 (1921), No. 2, pp. 37-43.
- Explosives: Some Properties of Explosives.** SIR ROBERT ROBERTSON. *Journal of the Chemical Society*, Vol. 119 (1921), No. 699, pp. 1-29.
- Fuel Oil: Heating by Fuel Oil for Manufacturing Processes.** C. C. HERMANN. *Industrial Management*, Vol. 61 (1921), No. 5, pp. 199-202.
- Fuels—Their Utilization and Conservation.** CHARLES LONGENECKER. *The Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 2, pp. 144-146.
- Gases: An Apparatus for Recording CO₂ and Combustible Gases.** ROLAND MOELLER. *Paper*, Vol. 27 (1921), No. 24, pp. 24-29.
- Gas Making with Cheap Oxygen.** E. A. W. JEFFERIES. *American Gas Engineering Journal*, Vol. 114 (1921), No. 9 (whole no. 3286), pp. 180-184, 189; *The Gas Age*, Vol. 47 (1921), No. 4, pp. 145-150.
- Glass: The Development of Various Types of Glass.** C. J. PEDDLE. *Journal of the Society of Glass Technology*, Vol. 4 (1920), No. 16, pp. 299-366.
- Glass: The Manufacture and Treatment of Glass Melting Pots.** W. K. BROWNLEE AND A. F. GORTON. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 2, pp. 97-112.
- Hardwood Distillation: "The Chemist and the Crude Factory" in the Hardwood Distillation Industry.** R. E. GILMORE. *Canadian Chemistry and Metallurgy*, Vol. 5 (1921), No. 2, pp. 37-41.
- Helium: Its History, Properties, and Commercial Development.** RICHARD B. MOORE. *Journal of the Franklin Institute*, Vol. 191 (1921), No. 2, pp. 145-197.
- Hydrocarbons: The Determination of Aromatic Hydrocarbons in Mixtures of Hydrocarbons.** H. T. TIZARD AND A. G. MARSHALL. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 3, pp. 201-254.
- Hydrogen: Possible Developments in Hydrogen Manufacture.** ERIC K. RIDEAL. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 2, pp. 101-141.
- Industrial Chemistry: Taking Industrial Chemistry into Partnership.** FREDERIC DANNER. *Industrial Management*, Vol. 61 (1921), No. 5, pp. 151-154.
- Lead Salts in the Cyanidation of Silver Ores.** RALPH W. PERRY. *Mining and Scientific Press*, Vol. 122 (1921), No. 7, pp. 221-225.
- Leather: Acid Unhairing.** R. H. MARRIOTT. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 1, pp. 2-10.
- Leather: Official Method of the American Leather Chemists' Association for the Analysis of Vegetable Materials Containing Tannin.** *Journal of the American Leather Chemists' Association*, Vol. 16 (1921), No. 3, pp. 113-139.
- Medicinals: Les Phénomènes Chimiques en Biologie et en Médecine.** H. SCHWARZ. *Chimie et Industrie*, Vol. 25 (1921), No. 1, pp. 18-26.
- Open Hearth Furnaces: Application of Waste Heat Boilers to Open Hearth Furnaces.** THOMAS R. TAYLOR. *The Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 2, pp. 173-174.
- Paper: The Compound Microscope and Its Value in the Mill.** I. L. GARTLAND. *Paper*, Vol. 27 (1921), No. 25, pp. 14-17, 36.
- Pharmaceutical Research.** GEORGE M. BERINGER. *Journal of the American Pharmaceutical Association*, Vol. 10 (1921), No. 2, pp. 89-96.
- Photography: Les Méthodes Actuelles de Virages en Diverses Couleurs des Papiers Photographiques aux Sels d'Argent.** A. SEYEWITZ. *Chimie et Industrie*, Vol. 5 (1921), No. 1, pp. 3-10.
- Potash: Sources and Composition of American Potash.** J. W. TURRENTINE. *The American Fertilizer*, Vol. 54 (1921), No. 5, pp. 93-104.
- Radio-Activity and Some Practical Applications.** C. W. DAVIS. *Mining and Scientific Press*, Vol. 122 (1921), No. 7, pp. 229-232.
- Rare Earths: The Precipitation of Some of the Rare Earths by Creams of Insoluble Oxides and Carbonates, Based on the Principle of Hydrolysis.** ARTHUR C. NEISH AND J. W. BURNS. *Canadian Chemistry and Metallurgy*, Vol. 5 (1921), No. 3, pp. 69-74.
- Research: The Value of Research in Mining and Metallurgy.** SAMUEL H. DOLBEAR. *Engineering and Mining Journal*, Vol. 111 (1921), No. 9, pp. 384-385.
- Steel: Notes on the Microstructure of Annealed Soft Steel, with Special Reference to Phosphorus in Tin Plate.** GEORGE F. COMSTOCK. *Forging and Heat Treating*, Vol. 7 (1921), No. 1, pp. 60-63.
- Steel: Review of Iron and Steel Literature, 1920.** E. H. McCLELLAND. *Forging and Heat Treating*, Vol. 7 (1921), No. 1, pp. 8-9.
- Sugar: Chemistry of Clarification in Plantation White Sugar Manufacture.** J. P. OGILVIE. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 2, pp. 22r-24r.
- Sugar: Clarifying Methods for Raw Sugar.** C. E. COATES. *Sugar*, Vol. 23 (1921), No. 3, pp. 149-150.
- Sulfite Liquors: Analysis of Sulfite Cooking Liquors.** A. CHAMBOVET. *Paper*, Vol. 27 (1921), No. 25, pp. 16-19. Translated from *La Papeterie*.
- Sulfuric Acid: Ammonia Oxidation Units for Sulfuric Acid Plants.** WILFRID WYLD. *The Chemical Age* (London), Vol. 4 (1921), No. 86, pp. 150-151.
- Sulfuric Acid: The Chamber Process under Tropical Conditions.** W. H. MAWDSLEY. *Chemical Trade Journal and Chemical Engineer*, Vol. 68 (1921), No. 1758, pp. 132-133.

MARKET REPORT—MARCH, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

	Mar. 1	Mar. 15
Acid, Boric, cryst., bbls.....lb.	.15	.14 1/2
Hydrochloric, com'l, 20°.....lb.	.017 1/2	.017 1/2
Hydriodic.....oz.	.19	.19
Nitric, 42°.....lb.	.071 1/2	.071 1/2
Phosphoric, 50% tech.....lb.	.20	.18
Sulfuric, C. P.....lb.	.07	.07
Chamber, 66°.....ton	20.00	20.00
Oleum 20%.....ton	23.00	23.00
Alum, ammonia, lump.....lb.	.041 1/4	.041 1/4
Aluminium Sulfate (iron-free).....lb.	.031 1/2	.03
Ammonium Carbonate, pwd.....lb.	.10	.08
Ammonium Chloride, gran.....lb.	.10	.10
Ammonia Water, carboys, 26°.....lb.	.09 3/4	.09 3/4
Arsenic, white.....lb.	.09	.08 1/2
Barium Chloride.....ton	65.00	65.00
Nitrate.....lb.	.14	.14
Barytes, white.....ton	30.00	30.00
Bleaching Powd., 35%, Works, 100 lbs.	3.50	3.50
Borax, cryst., bbls.....lb.	.071 1/2	.07
Bromine, tech. wks.....lb.	.40	.40
Calcium Chloride, fused.....ton	28.75	28.75
Chalk, precipitated, light.....lb.	.04	.04
China Clay, imported.....ton	18.00	18.00
Copper Sulfate.....100 lbs.	5.50	5.25
Feldspar.....ton	8.00	8.00
Fuller's Earth.....100 lbs.	1.00	1.00
Iodine, resublimed.....lb.	3.75	3.75
Lead Acetate, white crysta's.....lb.	.15	.15
Nitrate.....lb.	.15	.15
Red American.....100 lbs.	.11 1/4	.11 1/4
White American.....100 lbs.	.09 1/2	.09 1/2
Lim. Acetate.....100 lbs.	2.00	2.00
Lithium Carbonate.....lb.	1.50	1.40
Magnesium Carbonate, Tech.....lb.	.10 1/2	.10 1/2
Magnesite.....ton	72.00	72.00
Mercury flask.....75 lbs.	47.00	45.00
Phosphorus, yellow.....lb.	.35	.35
Plaster of Paris.....100 lbs.	1.50	1.50
Potassium Bichromate.....lb.	.13 3/4	.12 1/2
Bromide, Cryst.....lb.	.20	.18
Carbonate, calc., 80-85%.....lb.	.10	.08 1/2
Chlorate, cryst.....lb.	.08	.08
Hydroxide, 88-92%.....lb.	.11	.10
Iodide, bulk.....lb.	3.00	3.00
Nitrate.....lb.	.10	.10
Permanganate, U. S. P.....lb.	.50	.45
Salt Cake, Bulk.....ton	35.00	35.00
Silver Nitrate.....oz.	.40	.37 1/2
Soapstone, in bags.....ton	12.00	12.00
Soda Ash, 58%, bags.....100 lbs.	2.00	2.00
Caustic, 76%.....100 lbs.	3.60	3.65
Sodium Acetate.....lb.	.07	.07
Bicarbonate.....100 lbs.	2.00	2.00
Bichromate.....lb.	.08 1/2	.08
Chlorate.....lb.	.10	.10
Cyanide.....lb.	.20	.18
Fluoride, technical.....lb.	.14 1/4	.14 1/4
Hyposulfite, bbls.....100 lbs.	4.00	4.00
Nitrate, 95%.....100 lbs.	2.80	2.70
Silicate, 40°.....lb.	.011 1/2	.011 1/2
Sulfide.....lb.	.07	.07
Bisulfite, powdered.....lb.	.06	.06
Strontium Nitrate.....lb.	.15	.15
Sulfur, flowers.....100 lbs.	3.00	3.00
Crude.....long ton	20.00	20.00
Talc, American, white.....ton	18.00	18.00
Tin Bichloride.....lb.	.19 1/2	.19 1/2
Oxide.....lb.	.45	.40
Zinc Chloride, U. S. P.....lb.	.40	.40
Oxide, bbls.....lb.	.10	.10

ORGANIC CHEMICALS

Acetanilide.....lb.	.25	.28
Acid, Acetic, 28 p. c.....100 lbs.	3.00	2.75
Glacial.....lb.	.10	.09
Acetylsalicylic.....lb.	.65	.60
Benzoic, U. S. P., ex-toluene.....lb.	.70	.70
Carbolic, cryst., U. S. P., drs.....lb.	.11	.11
50- to 110-lb. tins.....lb.	.21	.21
Citric, crystals, bbls.....lb.	.45	.46

Acid (Concluded)

	Mar. 1	Mar. 15
Oxalic, cryst., bbls.....lb.	.18	.17 1/2
Pyrogallie, resublimed.....lb.	2.00	2.00
Salicylic, bulk, U. S. P.....lb.	.23	.23
Tartaric, crystals, U. S. P.....lb.	.32	.34
Trichloroacetic, U. S. P.....lb.	4.40	4.40
Acetone, drums.....lb.	.13 1/2	.13 1/2
Alcohol, denatured, 190 proof.....gal.	.58	.55
Ethyl, 190 proof.....gal.	4.90	4.90
Amyl Acetate.....gal.	3.50	3.05
Camphor, Jap. refined.....lb.	.80	.70
Carbon Bisulfide.....lb.	.08	.08
Tetrachloride.....lb.	.12	.12
Chloroform, U. S. P.....lb.	.40	.40
Creosote, U. S. P.....lb.	.55	.50
Cresol, U. S. P.....lb.	.18	.18
Dextrin, corn.....100 lbs.	3.55	3.55
Imported Potato.....lb.	.09	.09
Ether, U. S. P., conc., 100 lbs.....lb.	.20	.20
Formaldehyde.....lb.	.18	.15 1/2
Glycerol, dynamite, drums.....lb.	.16	.14 1/2
Methanol, pure, bbls.....gal.	1.65	1.25
Pyridine.....gal.	2.75	2.75
Starch, corn.....100 lbs.	2.65	2.65
Potato, Jap.....lb.	.05	.05
Rice.....lb.	.25	.25
Sago.....lb.	.05	.05

OILS, WAXES, ETC.

Beeswax, pure, white.....lb.	.55	.55
Black Mineral Oil, 29 gravity.....gal.	.22	.22
Castor Oil, No. 3.....lb.	.09 1/2	.09
Ceresin, yellow.....lb.	.13	.13
Corn Oil, crude.....lb.	.07 1/2	.07 1/2
Cottonseed Oil, crude, f. o. b. mill.....lb.	.05	.04 3/4
Linseed Oil, raw.....gal.	.67	.67
Menhaden Oil, crude (southern).....gal.	.30	.30
Neat's-foot Oil, 20°.....gal.	1.15	1.15
Paraffin, 128-130 m. p., ref.....lb.	.08	.08
Paraffin Oil, high viscosity.....gal.	.45	.45
Rosin, "F" Grade, 280 lbs.....bbl.	7.00	6.25
Rosin Oil, first run.....gal.	.48	.45
Shellac, T. N.....lb.	.55	.48
Spermaceti, cake.....lb.	.30	.30
Sperm Oil, bleached winter, 38°.....gal.	1.73	1.73
Stearic Acid, double-pressed.....lb.	.12	.11 1/2
Tallow Oil, acidless.....gal.	.82	.80
Tar Oil, distilled.....gal.	.60	.60
Turpentine, spirits of.....gal.	.61	.60

METALS

Aluminium, No. 1, ingots.....lb.	.24	.23
Antimony, ordinary.....100 lbs.	5.25	5.75
Bismuth.....lb.	1.75	1.65
Copper, electrolytic.....lb.	.12 3/4	.12
Lake.....lb.	.13	.12 1/4
Lead, N. Y.....lb.	.04	.04 1/4
Nickel, electrolytic.....lb.	.45	.45
Platinum, refined, soft.....oz.	65.00	65.00
Quicksilver, flask.....75 lbs ea.	47.00	45.00
Silver.....oz.	.56 1/2	.57
Tin.....lb.	.30	.28
Tungsten Wolframite.....per unit	3.50	3.25
Zinc, N. Y.....100 lbs.	5.10	5.10

FERTILIZER MATERIALS

Ammonium Sulfate export.....100 lbs.	3.25	3.25
Blood, dried, f. o. b. N. Y.....unit	3.50	3.50
Bone, 3 and 50, ground, raw.....ton	45.00	45.00
Calcium Cyanamide, unit of Ammonia.....	4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works.....unit	3.50 & .10	3.50 & .10
Phosphate Rock, f. o. b. mine:		
Florida Pebble, 68%.....ton	11.00	11.00
Tennessee, 78-80%.....ton	15.00	15.00
Potassium Murate, 80%.....unit	1.40	1.35
Pyrites, furnace size, imported.....unit	.18	.18
Tankage, high-grade, f. o. b. Chicago.....unit	2.75 & .10	2.75 & .10

COAL-TAR CHEMICALS

	Mar. 1	Mar. 15
Crudes		
Anthracene, 80-85%.....lb.	.75	.75
Benzene, Pure.....gal.	.30	.30
Cresol, U. S. P.....lb.	.18	.18
Cresylic Acid, 97-99%.....gal.	.90	.90
Naphthalene, flake.....lb.	.08	.08
Phenol, drums.....lb.	.10	.10
Toluene, Pure.....gal.	.30	.30
Xylene, 2 deg. dist. range.....gal.	.60	.60

Intermediates

Acids:		
Anthranilic.....lb.	2.20	1.80
B.....lb.	2.25	2.25
Benzoic.....lb.	.60	.60
Broenner's.....lb.	1.75	1.75
Cleve's.....lb.	1.50	1.50
Gamma.....lb.	3.75	3.75
H.....lb.	1.25	1.25
Metanilic.....lb.	1.60	1.60
Monosulfonic F.....lb.	2.75	2.75
Naphthionic, crude.....lb.	.75	.75
Neville & Winther's.....lb.	1.60	1.60
Phthalic.....lb.	.40	.40
Picric.....lb.	.30	.30
Sulfanilic.....lb.	.33	.33
Tobias.....lb.	2.25	2.25
Aminoazobenzene.....lb.	1.25	1.25
Aniline Oil.....lb.	.22	.22
For Red.....lb.	.42	.42
Aniline Salt.....lb.	.28	.28
Anthraquinone.....lb.	2.00	2.00
Benzaldehyde, tech.....lb.	.45	.45
U. S. P.....lb.	1.00	1.00
Benzidine (Base).....lb.	.90	.90
Benzidine Sulfate.....lb.	.75	.75
Diaminophenol.....lb.	5.50	5.50
Dianisidine.....lb.	6.00	6.00
p-Dichlorobenzene.....lb.	.15	.15
Diethylaniline.....lb.	1.40	1.40
Dimethylaniline.....lb.	.50	.50
Dinitrobenzene.....lb.	.25	.25
Dinitrotoluene.....lb.	.28	.28
Diphenylamine.....lb.	.60	.60
G Salt.....lb.	.80	.80
Hydroquinol.....lb.	1.70	1.70
Metol (Rhodol).....lb.	6.75	6.75
Monochlorobenzene.....lb.	.14	.14
Monothylaniline.....lb.	2.15	2.15
o-Naphthylamine.....lb.	.38	.38
o-Naphthylamine (Sublimed).....lb.	2.25	2.25
o-Naphthol, dist.....lb.	.34	.34
m-Nitroaniline.....lb.	.90	.90
p-Nitroaniline.....lb.	.90	.85
Nitrobenzene, crude.....lb.	.13	.13
Rectified (Oil Mirbane).....lb.	.14 1/2	.14
p-Nitrophenol.....lb.	.80	.80
p-Nitrosodimethylaniline.....lb.	2.90	2.90
o-Nitrotoluene.....lb.	.25	.25
p-Nitrotoluene.....lb.	.90	.90
m-Phenylethylenediamine.....lb.	1.15	1.15
p-Phenylenediamine.....lb.	1.75	1.75
Phthalic Anhydride.....lb.	.55	.55
Primuline (Base).....lb.	3.00	3.00
R Salt.....lb.	.80	.75
Resorcinol, tech.....lb.	2.00	2.00
U. S. P.....lb.	2.25	2.25
Schaeffer Salt.....lb.	.75	.70
Sodium Naphthionate.....lb.	1.10	1.10
Thiocarbanilide.....lb.	.60	.60
Tolidine (Base).....lb.	1.40	1.40
Toluidine, mixed.....lb.	.44	.44
o-Toluidine.....lb.	.27	.27
m-Toluylenediamine.....lb.	1.15	1.15
p-Toluidine.....lb.	1.25	1.25
Xylidine, crude.....lb.	.45	.45

COAL-TAR COLORS

Acid Colors		
Black.....lb.	1.00	1.00
Blue.....lb.	1.50	1.50

Acid Colors (Concluded)		
Fuchsin.....lb.	2.50	2.50
Orange III.....lb.	.60	.60
Red.....lb.	1.30	1.30
Violet 10B.....lb.	6.50	6.50
Alkali Blue, domestic.....lb.	6.00	6.00
Imported.....lb.	8.00	8.00
Azo Carmine.....lb.	4.00	4.00
Azo Yellow.....lb.	2.00	2.00
Erythrosin.....lb.	7.50	7.50
Indigotin, conc.....lb.	2.50	2.50
Paste.....lb.	1.50	1.50
Naphthol Green.....lb.	1.95	1.95
Ponceau.....lb.	1.00	1.00
Scarlet 2R.....lb.	.85	.85

Direct Colors

Black.....lb.	.90	.90
Blue 2B.....lb.	.70	.70
Brown R.....lb.	1.65	1.65
Fast Red.....lb.	2.35	2.35
Yellow.....lb.	2.00	2.00
Violet, conc.....lb.	1.10	1.10
Chrysophenine, domestic.....lb.	2.00	2.00
Congo Red, 4B Type.....lb.	.90	.90
Primuline, domestic.....lb.	3.00	3.00

Oil Colors

Black.....lb.	.70	.70
Blue.....lb.	.80	.80
Orange.....lb.	1.40	1.40
Red III.....lb.	1.65	1.65
Scarlet.....lb.	1.00	1.00
Yellow.....lb.	1.25	1.25
Nigrosine Oil, soluble.....lb.	.90	.90

Sulfur Colors

Black.....lb.	.20	.20
Blue, domestic.....lb.	.70	.70
Brown.....lb.	.35	.35
Green.....lb.	1.00	1.00
Yellow.....lb.	.90	.90

Chrome Colors

Alizarin Blue, bright.....lb.	5.00	5.00
Alizarin Red, 20% Paste.....lb.	1.10	1.10
Alizarin Yellow G.....lb.	1.00	1.00
Chrome Black, domestic.....lb.	1.25	1.25
Imported.....lb.	2.20	2.20
Chrome Blue.....lb.	1.00	1.00
Chrome Green, domestic.....lb.	1.50	1.50
Chrome Red.....lb.	2.00	2.00
Gallocyanin.....lb.	2.80	2.80

Basic Colors

Auramine, O, domestic.....lb.	2.50	2.50
Auramine, OO.....lb.	4.15	4.15
Bismarck Brown R.....lb.	.80	.80
Bismarck Brown G.....lb.	1.00	1.00
Chrysoidine R.....lb.	.75	.75
Chrysoidine Y.....lb.	.75	.75
Green Crystals, Brilliant.....lb.	3.50	3.50
Indigo, 20 p. c. paste.....lb.	.85	.85
Fuchsin Crystals, domestic.....lb.	4.50	4.50
Imported.....lb.	12.00	12.00
Magenta Acid, domestic.....lb.	4.25	4.25
Malachite Green, crystals.....lb.	2.75	2.75
Methylene Blue, tech.....lb.	2.75	2.75
Methyl Violet 3 B.....lb.	2.75	2.75
Nigrosine, spts. sol.....lb.	.70	.70
Water sol., blue.....lb.	.60	.60
Jet.....lb.	.90	.90
Phosphine G., domestic.....lb.	7.00	7.00
Rhodamine B, extra conc.....lb.	16.00	16.00
Victoria Blue, base, domestic.....lb.	6.00	6.00
Victoria Green.....lb.	2.50	2.50
Victoria Red.....lb.	7.00	7.00
Victoria Yellow.....lb.	7.00	7.00

The First Book In The Series of
American Chemical Society
MONOGRAPHS



*140 Pages 6 x 9
 size, stiff covers,
 bound in dark
 blue cloth,
 stamped in gold.*

PRICE
\$2.50

The
CHEMISTRY of ENZYME ACTIONS

By
K. GEORGE FALK

NOW READY

CONTENTS:

I. Introduction. II. Velocities of chemical reactions. III. General theory of chemical reactions; catalysis. IV. Chemical reactions catalyzed by enzymes. V. Physical properties common to enzyme preparations. VI. Chemical properties common to enzyme preparations. VII. Chemical nature of certain enzymes. VIII. Mechanism of enzyme actions. IX. Uses and applications of enzymes. X. Present status of enzyme problem. Index.

The Monograph Series

BY arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects.

Dr. Falk's book is the first in this series, of which there are already eleven others now being written or printed.

The publication of these monographs marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped therefore that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

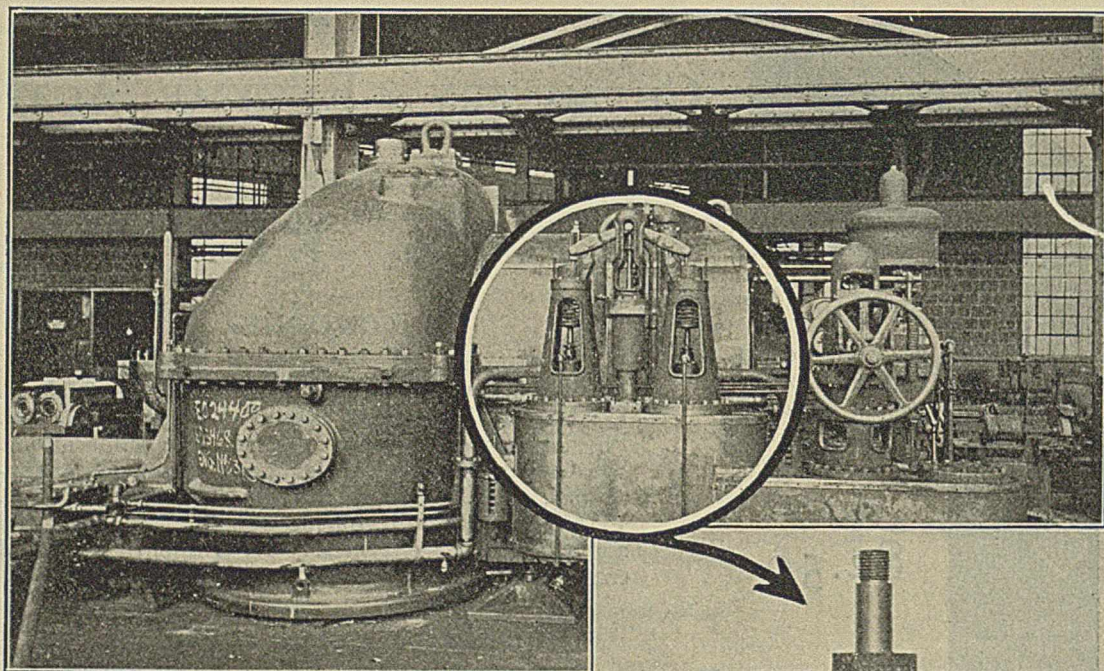
For additional information regarding this series, write to the Chemical Catalog Company.

*As the number of copies of Dr. Falk's monograph
 will be limited your early reservation is solicited.*

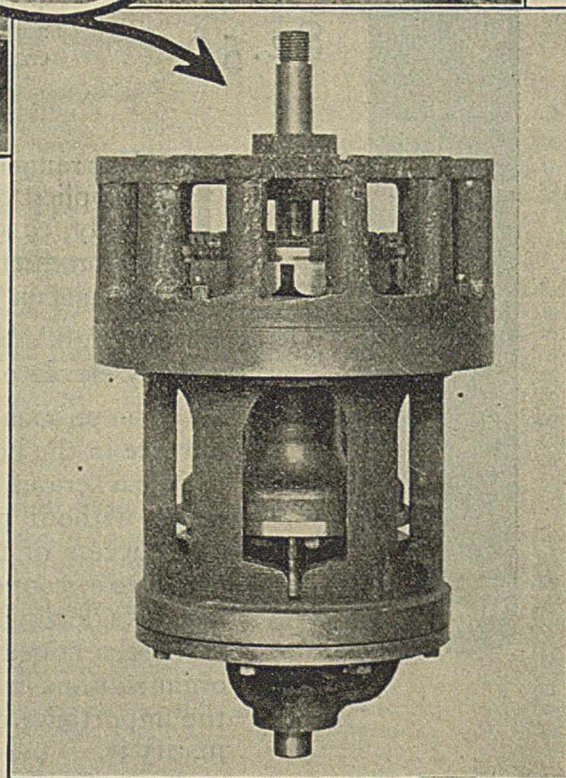
The **CHEMICAL CATALOG COMPANY, Inc.**
 ONE MADISON AVENUE, NEW YORK, U. S. A.

A FEW MONEL USES

Valves	Pumps	Meters	Gas and Oil Engines	Gauges
Seats	Pump Liners	Cylinders	Valves	Pins
Rings	Runners	Bushings	Ignition Chambers	Pivots
Guide Stems	Valve Seats	Valves	Ignition Tubes	Diaphragms
Clappers	Trim	Valve Parts	Fuel Filters	
Wedges	Hand Hole Covers	Spindles	Scavenger Valves	
Spindles	Plunger Rods	Screws		
Dash Pots	Stuffing Boxes	Gear		
Pistons	Plungers	Wheels		
			Turbines	Conveying and Handling Apparatus
			Poppet Valve Parts	Chains
			Blading	Buckets
				Hoppers



Westinghouse 128 C.W. 10,000 K.W. Turbine. Arrow indicates detail of valve in which Monel metal fittings are used.



THE INTERNATIONAL NICKEL COMPANY

Producers of METALLIC NICKEL in the forms of Ingot, Shot, Electrolytic Cathodes-99⁸/₁₀%, Malleable Nickel, NICKEL SALTS Oxides, Carbonates, Sulphates, Sulphides, Acetates, Formates - MONEL METAL Ingot, Shot, Blocks.