The Journal of Industrial and Engineering Chemistry

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EDITORIALS

THE SPRING MEETING AT CINCINNATI

The Forty-ninth Meeting of the American Chemical Society convened in Cincinnati, April 6th–10th; the total registration was 658. The sessions were held at the University of Cincinnati, twenty minutes' ride from the headquarters at the Hotel Sinton.

The business meeting of the Council on Monday evening was devoted to committee reports. The report of the Supervisory Committee on Standard Methods of Analysis was discussed at length. A tentative report of the special Committee on Business Management was made by Prof. Baskerville. After some discussion it was accepted as a report of progress and the committee was requested to submit it, with a statement of the reasons for and against the plan proposed, to the Council and local sections before May 15th, in order that final action may be taken at the Annual Meeting at Montreal this fall.

The formal opening of the convention was the General Meeting in McMicken Hall, where the Society was welcomed by the Honorable F. S. Spiegel, Mayor of Cincinnati, and by President Charles W. Dabney of the University of Cincinnati. President T. W. Richards responded to their cordial greetings and congratulated the Society on the recently made statement that the twentieth century is to be a chemical century. The scientific program is printed in full in this issue.

The Local Executive Committee, consisting of F. W. Weissmann, Stephen J. Hauser and Archibald Campbell, deserve the unbounded gratitude of the Society for the manner in which they handled the many details of the meeting. Arrangements were made with the University of Cincinnati for serving luncheon each day at the University, and this was of special convenience to those taking part in the many excursions. These trips were in charge of Mr. G. Farnham and included the inspection of twenty-four important industrial plants and points of interest in the vicinity of Cincinnati, and visits to the National Cash Register Factory at Dayton, Ohio, and the American Rolling Mills at Middletown, Ohio. Special street cars or automobiles were furnished so that the minimum fatigue might result from the inspection of large plants. Special trains took the visitors to the Dayton and Middletown factories. Further details as to these instructive and enjoyable excursions will be found elsewhere in this Journal.

On Tuesday evening, the complimentary smoker was given at the Hotel Sinton. Ample supplies of food and favorite drinks were served along with choice brands of "smokes;" the members were provided with colored tissue paper caps which added to the gaiety of the occasion. Mr. E. B. Remelin humorously demonstrated the simplicity of several Modern Chemical Developments including the manufacture of synthetic rubber, the ease with which radium may be prepared in large quantities (according to methods developed by Prof. Parsons) and its use in the rapid cure of malignant cancer. A cartoonist sketched favorite poses and well-known characteristics of prominent personalities in the Society, and the entertainment was concluded by a number of deft and pleasing sleight-of-hand tricks. Mr. Broeman and his committee received the thanks of all present for a most successful evening.

A notable entertainment was furnished by the Cincinnati Symphony Orchestra in a complimentary concert tendered to the visiting members of the Society by the Cincinnati Section at the Emery Auditorium on Wednesday evening with Dr, Ernst Kunwald conducting and Mr. Emil Heermann as violin soloist.

PROGRAM.

1. Overture—"Der Freischütz"........................ *Weber*
2. "Unfinished" Symphony......................... *Schubert*
3. Hungarian Rhapsody No. 1 .... *Liszt*
4. Concerto Grosso No. 6............................ *Haendel*
   Dr. Kunwald at the Piano.
5. Violin Concerto.................................... *Bach*
   Emil Heermann.
6. Academische Fest Overture........................ *Brahms*

The program was rendered with a sympathy and delicacy of musical feeling that only careful training, finished technique and perfect ensemble work can make possible. The enjoyment of the audience was attested by hearty applause and appreciative compliments from the many music lovers in the Society.

Previous to the Symphony Concert the abstractors and editors of the Society's Journals were served an excellent dinner in the dining room of the Ohio Mechanics Institute. Various suggestions as to the improvement and more extended distribution of the Society Journals were informally discussed. About thirty guests were present and it is hoped that such meetings of our editorial force may become an integral part of our general meetings, since they will afford an excellent stimulus to the coöperation necessary for the best success of the Society's publications.

The Banquet on Thursday evening at the Hotel Sinton was attended by over two hundred guests. The large banquet hall was artistically decorated with pink carnations, ferns and smilax, and an exquisite musical program was rendered during the evening. Prof. Wilder D. Bancroft acted as Toastmaster and addresses were made by Charles W. Dabney, Theodore W. Richards, Albert Bettinger and John Uri Lloyd. The Society owes much to the Banquet Committee, headed by Mr. Lauder W. Jones, for bringing the Cincinnati part of the meeting to a close with such a delightful social function.

Ladies to the number of one hundred and twenty-five attended the meeting. Their comfort and enjoyment were provided for by a large committee under the efficient leadership of Mrs. J. W. Ellms. About seventy guests attended the complimentary dinner

DELEGATES OF THE FORTY-NINTH MEETING OF THE AMERICAN CHEMICAL SOCIETY AT THE NATIONAL CASH REGISTER PLANT, DAYTON

served to the ladies at the Hotel Sinton on Tuesday evening when interesting talks were made by some of the members and several of the guests who had been connected with pure food campaigns in the large cities. The dinner was followed by a very enjoyable theatre party to which the guests were conveyed in automobiles. Wednesday was spent at Ft. Thomas and Thursday at the Rookwood Pottery. All of the regular division meetings and excursions were open to the ladies. A large number took the Dayton-Middletown trip, the ride thence being shortened by piano and vocal solos as well as folk songs in which the entire party joined.

The industrial activity of the Queen City of the West, the use of its University for the meetings, the hospitality of the many institutions and factories so graciously thrown open, the general comfort brought about by the skillful planning of the committees of the Local Section, will linger long in the memories of those who attended the Spring Meeting at Cincinnati.

JOURNAL OF THE AMERICAN WATER WORKS ASSOCIATION

We have just received the first number, March, 1914, of the *Journal of the American Water Works Association*. This Journal is to take the place of the annual proceedings, and marks a great step in advance in the affairs of the Association, which is now thirty-four years old. At the last convention of the Association, a new constitution was adopted giving it an organization resembling, in several features, that of the American Chemical Society. The formation of sections was authorized, and already a New York Section has been formed that has had two successful meetings. The expansion under the new constitution requires a more prompt medium for the production of the proceedings and papers and therefore, the executive committee of the Association has established a quarterly journal.

It is planned to issue the first number each year before the annual convention. It will contain papers, which will later be discussed at the convention. A second number will contain the proceedings of the convention and such papers and discussions as may be promptly available for publication. The third and fourth numbers will contain the remaining papers and discussions from the annual convention, publish additional papers submitted to the sections, make necessary announcements of local meetings and contain a revised list of members.

By this procedure the Association will present its papers more promptly, avoiding the delays attendant on a single annual issue. The Journal will furnish a repository for water works literature, which will bring it in closer touch with the needs and interests of the membership, besides offering a greater incentive to contributors.

The first number contains nine papers. From the character of these we see that the new journal will deal with matters of interest to a large variety of readers including chemists, bacteriologists, engineers, administrators, and practical water works operators.

We hope that this new departure will make the American Water Works Association a greater benefit than ever before to its members.

THE DISTRIBUTION OF INDUSTRIES

In a communication to the National Liberal Immigration League, Dr. C. W. Eliot presents his remedy for municipal congestion. In his opinion, the prevention of the overcrowding of our industrial centers and the evils attending this overcrowding lies not in restricting immigration, but in the distribution of industrial plants throughout the country.

This is a matter which has already received considerable attention by economists, though not as exhaustively as it might deserve, if the fundamental conditions did not require so radical a change to make it practicable. The main factor which attracts industries in American cities is the concentration of lines of transportation at those points. Were transportation rates always as low at rural points as at the cities, the task would be greatly simplified. Doctor Eliot is of the opinion that the project is now easier

because of the parcel post development, the growth of trolley lines, and freight and automobile trucks. However, industrial growth will depend on cheap railroad rates for fuel and raw materials and for shipment of finished products to a degree which will make the other means of transportation hardly worthy of consideration.

On the other hand, there are certain characteristics in rural locations which are attractive for industrial enterprises. The cost of sites for factories and residences of employees, the ability of workingmen to have their own gardens, the facility for waste disposal, can, if the fundamental conditions be made right, work a practical revolution. But transportation conditions are the vital point and the scheme will be impracticable until the rural point can be guaranteed the same transportation rates as the city.

W. A. HAMOR

NEW SECTION ADDED TO JOURNAL

A new section on GOVERNMENT PUBLICATIONS has been added to the JOURNAL, beginning in this issue, under the editorship of R. S. McBride, Associate Chemist in the Bureau of Standards. This work is planned to bring to chemists and engineers prompt notice of all government reports of interest to them, and to briefly and clearly review the scope and purpose of these publications. It is not intended that the articles shall be fully abstracted, since the work of *Chemical Abstracts* in this line should not be duplicated; but a prompt announcement of the publications will do a great deal to assist the chemical profession in taking advantage of the material now being issued by the Government. It will certainly be more convenient for the members of our Society thus to have condensed into one list the announcements previously scattered through a number of lists appearing at irregular intervals from the various departments. All Government Printing Office publications of value to chemists will be reviewed, including those which have appeared since January 1, 1914. The items of industrial importance appearing in the *Daily Consular Reports* will also be abstracted, beginning with March 1, 1914.

It is our belief that this up-to-date summary of the important investigations and publications of the Government will be of immense value to our profession.

ORIGINAL PAPERS

STUDY OF THE COMPOSITION OF WATER GAS TAR

By C. R. Downs and A. L. Dean
Received February 17, 1914

Water gas tar, more properly carburetted water gas tar, is the tarry product separating out in the purifying systems of plants manufacturing carburetted water gas. It is much less viscous than ordinary coal tar, with a distinctly different odor, due in part to the absence of the phenols and bases characteristic of coal tar. It is understood that a portion of the petroleum used in carburetting, after passing through various molecular changes, appears finally as tar, but of the exact nature of the transformations little is definitely known. It is, of course, the object of the gas maker to change as large a percentage of his gas oil into permanent gases as possible and keep the production of tar to the lowest limit.

A search through the literature for data concerning water gas tar yields but fragmentary and inadequate results. A. H. Elliott,[1] Matthews and Goulden,[2] and C. N. Forrest[3] have recorded the results of fractional distillations of the tar, and Dean and Bateman,[4] S. P. Sadtler,[5] and Forrest[3] have furnished information regarding the composition of the creosote oils derived from water gas tar. Some of the statements to be found in the literature refer to material clearly quite different from the water gas tar produced in the standard American installations of the present day. Thus Matthews and Goulden's tar was lighter than water and contained 8.51 per cent of "light paraffins."

The data presented in this paper were obtained on water gas tar from the purifying system served by several standard Lowe system water gas sets. The carburetting oil in use at the time was derived from Oklahoma crudes. As might be predicted, the tar separating at different points along the purifying system, as the gas passes from the sets to the final stages of purification, becomes progressively lighter and richer in the more volatile constituents.[1] Mixed tar from the whole system was used for the work described in the present paper.

SYSTEMATIC FRACTIONAL DISTILLATIONS

A series of detailed fractional distillations was carried out with a view to locating the boiling points of any individual compounds which might be present in substantial amounts. The first distillation of the tar up to 250° C. was carried out in a five gallon
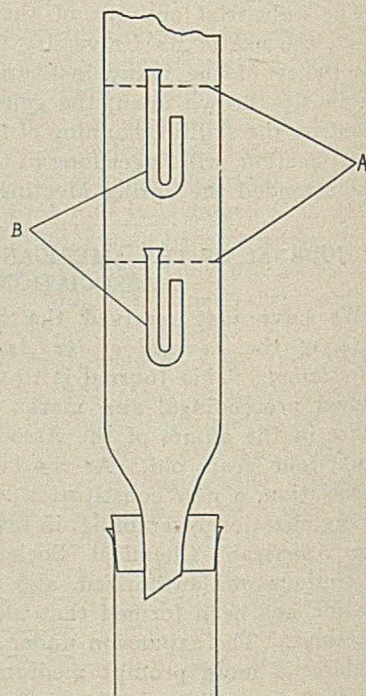
FIG. 1—CHAMBERS OF DEPHLEGMATOR
A, PERFORATED GLASS PLATES
B, SIPHON TUBES

[1] *Am. Chem. Jour.*, **6**, 248.
[2] *Gas World*, **16**, 625.
[3] *Jour. Soc. Chem. Ind.*, **30**, 193.
[4] U. S. Forest Service, *Circular* **112**.
[5] *Trans. Am. Inst. Chem. Eng.*, **2**, 177.

[1] Dean and Downs, THIS JOURNAL, **3**, 108.

copper still, the distillation being effected by immersing a resistance coil in the tar. The distillates thus obtained constituted the "First Series" of fractions, and the
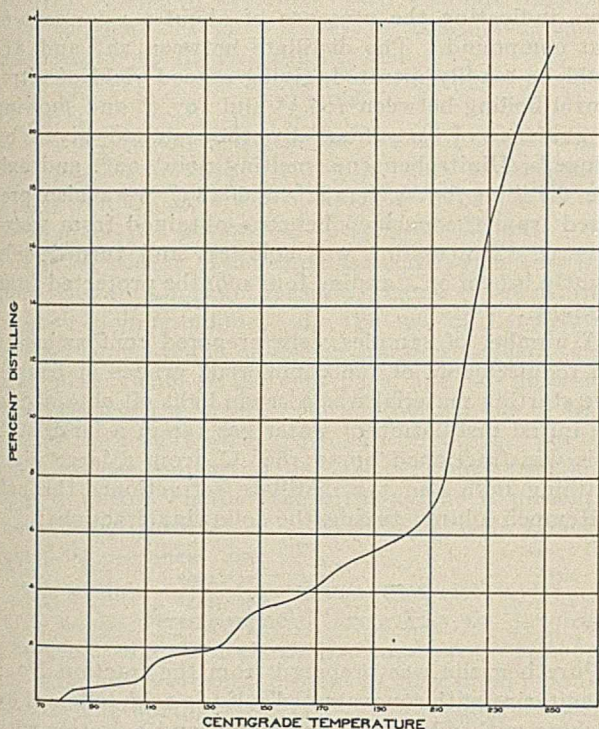
FIG. 2—THIRD SERIES DISTILLATION

residue was saved for later study. These first fractions were then refractioned from an electrically heated glass flask provided with a Hempel column, yielding the "Second Series." In refractioning the second and subsequent distillates a modified Young dephlegmator was employed up to 200° C., and above that the Hempel column. This Young dephlegmator consisted of six chambers, the floors of which consisted of perforated glass plates provided with overflow tubes as
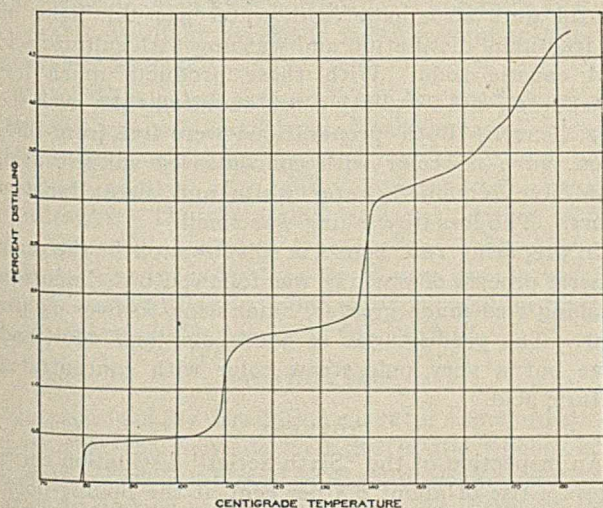
FIG. 3—SIXTH SERIES DISTILLATION

indicated in Fig. 1. To avoid excessive condensation in the chambers the dephlegmator was air-jacketed up to 110° C., and above that enclosed in an asbestos sheath heated by resistance wires. In this way the process of repeated fractionation, according to the

common practice of handling the fractions in such work, was continued to the "Third Series" of fractions boiling up to 250° C. and to the "Sixth Series" with the lower boiling portions. The curves of the third and sixth series are shown in Figs. 2 and 3.

From Fig. 2 it is clear that the largest single constituent boils at about 220° C., approximately the boiling point of naphthalene. The abrupt rises in Fig. 3 at 80°, 110° and 140° C. indicate the presence of appreciable amounts of individual substances boiling near these temperatures, which were subsequently proven to be benzene, toluene, and the xylenes. A smaller irregularity appears near the boiling point of mesitylene, 164.5° C. It is believed that a fairly satisfactory separation had been achieved in this sixth series, and during considerable portions of the distillation when the distillates appeared to be nearly pure compounds, fractions were taken at each degree rise in temperature and corrections made for the emergent thermometer stem.

GENERAL CHARACTERISTICS OF THE DISTILLATES

INDICES OF REFRACTION—The indices of refraction of the fractions of the fifth series were determined at 30° C. with the results shown in the following table:

Temp. of fraction ° C.	Refractive index at 30° C.	Temp. of fraction ° C.	Refractive index at 30° C.
79– 83	1.4938	125–130	1.4916
83– 85	1.4938	130–137	1.4935
85– 90	1.4933	137–145	1.4967
90– 95	1.4923	145–150	1.4987
95–100	1.4921	150–155	1.4976
100–109	1.4910	155–160	1.4968
109–113	1.4909	160–165	1.4979
113–115	1.4910	165–172	1.5030
115–120	1.4908	172–179	1.5180
120–125	1.4912	179–185	1.5269

BROMINE ABSORPTION

The bromine absorptions of the fractions were used as a relative measure of the unsaturated hydrocarbons. The determinations were made by allowing an excess of a tenth normal solution of bromine in carbon tetra-

Sixth series fractions ° C.	G. Br added per cc.	Third series fractions ° C.	G. Br added per cc.
78.9– 79.7	0.0133	180–205	0.4487
79.7– 80.7	0.0181	205–235	0.2526
80.7– 85.0	0.0133	235–250	0.1629
85.0– 92.0	0.0182		
92 –101	0.0192	Second series	
101 –109	0.0141	fractions	
109 –110.5	0.0104	250–260	0.0479
110.5–114	0.0133	260–270	0.0432
114 –120	0.0247	270–280	0.0610
120 –130	0.0364	280–290	0.0442
130 –138	0.0671	290–300	0.0963
138 –142.5	0.1098	300–310	0.0771
142.5–145	0.1724	310–320	0.0700
145 –150	0.2186		
150 –155	0.1832		
155 –160	0.1616		
160 –164	0.1522		
164 –167	0.4176		
167 –172	0.4824		
172 –177	0.4008		
177 –182	0.5520		

chloride to react on 1 cc. of a sample for 15 minutes, the vessel containing the mixture being immersed in a bath of ice and salt and kept in the dark. After this

reaction period the unused bromine and the hydrobromic acid formed were both determined, and from these determinations the grams of bromine added per cubic centimeter of oil could readily be calculated.

"PARAFFINS"

Since the hydrocarbons of water gas tar have their origin in petroleum oil it might be supposed that considerable quantities of "paraffins" would be found in the distillate therefrom. To throw light on this point the fractions were sulfonated with concentrated sulfuric acid and the percentage by volume of the unsulfonated residues determined.

Temp. of fraction 6th series	Per cent Unsulfonated	Temp. of fraction 6th series	Per cent unsulfonated
75 – 79	0.06	138 –142.5	1.2
79 – 90	None	142.5–145	2.4
80 – 81	None	145 –150	1.2
81 – 85	None	150 –155	2.2
85 – 92	None	155 –161	1.6
92 –101	None	161 –166.5	1.8
101 –109	None	166.5–172	1.6
109 –110.5	None	172 –177	None
110.5–114	None	3rd series	
114 –120	None	180 –205	55.0
120 –130	0.4	205 –235	1.4
130 –138	0.4	235 –250	2.2

The extraordinarily high percentage in the distillate from 180°–205° calls for some comment. The residues from all the other fractions were washed to clear oils, but the material obtained here was of putty-like consistency and resinous odor, and appeared to be a polymerization product of some unsaturated hydrocarbon rather than a "paraffin."

LOW-BOILING FRACTION

On repeated distillation of the first fractions below 75° C. a small amount of a very volatile liquid was obtained, boiling between 44° C. and 65° C., most of it coming over between 60° and 62°.

So small a quantity of this material was obtained that anything more than a few qualitative tests was not feasible. It charred and left no residue of undissolved oil when treated with concentrated sulfuric acid. It reacted violently with strong nitric acid, and absorbed bromine rapidly from bromine water, forming a brominated product heavier than water. No test for sulfur could be obtained. These tests combine to indicate a hydrocarbon mixture of markedly unsaturated character.

THIOPHEN

The sulfur containing compound thiophen (C_4H_4S) appears to be always associated with benzol in coal tar light oil. Because of the closeness of its boiling point (84° C.) to that of benzol, it cannot be removed by fractional distillation. The presence of thiophen in water gas tar distillates was indicated by the indophenine test with isatin and concentrated sulfuric acid. The method of Denigès[1] was followed in making quantitative estimations of this compound. The average of thirteen analyses of the fractions between 79° C. and 90° C. was 2.1 per cent.

Tests for the higher homologues of thiophen were obtained with the higher boiling fractions, but no quantitative estimations were attempted.

[1] *Compt. rend.*, **90**, 781.

BENZENE

An inspection of the distillation curve of the sixth series shows a decided rise at the boiling point of benzene, indicating the presence of about 0.4 per cent of that compound. The distillate between 79° and 81° could be readily nitrated, giving a good yield of nitrobenzol boiling between 106.5° and 107.5° and showing no evidence of "paraffins" by the method given by Lunge.[1] Dinitrobenzene, melting point 90°, and aniline distilling between 182° and 185° were also prepared from the purified benzene obtained from water gas tar. The aniline was colorless and turned only slightly brown on standing four months protected from sunlight.

A number of samples were prepared conforming to the requirements of the commercial grades of benzol. The starting material was a crude light oil obtained in the initial distillation of water gas tar in a large still. This was fractioned up to 180° C. from a large plain distilling bulb and the distillate refractioned through a Hempel column taking the following fractions:

1.	68°– 79°
2.	79°–100°
3.	100°–125°
4.	125°–155°

Pure benzene was prepared from the fraction No. 2 by agitating with concentrated sulfuric acid, followed by washing with dilute acid and water, and agitation with caustic soda solution followed by thorough washing. Under laboratory conditions a loss of 4 per cent was experienced by these treatments. The washed product was carefully redistilled with a Hempel column and Young dephlegmator, yielding a product of correct boiling point. This c. p. benzene gave no test for thiophen, no discoloration with concentrated sulfuric acid, was of sweet odor and has shown no yellowing on standing for two years.

Preparations of 90 per cent benzol and 50 per cent benzol were also made from water gas tar light oil by fractional distillation and washing with sulfuric acid and caustic soda. With these products much less exact fractional distillation was required than with the c. p. benzol. Both preparations were free from thiophen, gave no color with concentrated sulfuric acid, and have remained water white and sweet for two years. The loss in washing was small.

In preparing 160° benzol or solvent naphtha the same general process of washing was followed but the loss in washing was much greater, amounting to over 15 per cent. The product was of good color and odor, and gave but a very pale straw color with concentrated sulfuric acid.

TOLUENE

An inspection of the "Sixth Series" distillation curve shows a rise of about 0.8 per cent at the boiling point of toluene. A portion of this fraction of the sixth series was nitrated, giving 85 per cent of the theoretical yield, and showing but a trace of paraffins.

The fraction No. 3 from the Hempel column distillation mentioned under "Benzene" above was washed with sulfuric acid and alkali (with a loss of 6 per cent)

[1] "Coal Tar and Ammonia," 3rd Edition, p. 641.

and the washed oil fractioned with a Hempel column. The fraction 95°–120° was redistilled with the same apparatus and the fraction 109.5°–111.5° taken. This product compared favorably with standard makes of c. p. toluene and gave no test for thiotoluene and no color with concentrated sulfuric acid.

XYLENES

The next decided rise in the distillation curve after that at the toluene fraction appears around 140°, suggesting the presence of xylenes. The curve indicated about 1.2 per cent of these hydrocarbons.

The separation of the three isomeric xylenes by fractional distillation is not feasible because of the nearness of their boiling points. By the use of Levenstein's method[1] one sample of xylene fraction yielded 75 per cent metaxylene, 20 per cent para, and, by difference, 5 per cent of the ortho. On another sample of water gas tar the results were 77 per cent meta, 19.5 per cent para, 2.0 per cent ortho, and 1.5 per cent "paraffins." It is doubtful whether the ortho-xylene is present in more than traces since a qualitative test[2] failed to reveal its presence.

The sodium salts of the ortho- and meta-xylene sulfuric acids were prepared according to Jacobsen.[3] The needle-like crystals similar to those described for the ortho salt were only present in very small amounts. Metaxylene boiling 138°–139° was prepared according to Jacobsen by decomposing the meta-xylene sulfuric acid.

MESITYLENE

A slight irregularity of the distillation curve around 165° suggested the presence of mesitylene. The "Sixth Series" distillate obtained at this point was twice redistilled with a Glinsky dephlegmator and the distillate between 164° and 167° nitrated. A solid nitro-compound was obtained which after careful washing and recrystallization gave a constant melting point of 236°. The nitration of another portion gave a product melting at 235°. Mulliken gives the melting point of trinitro mesitylene as 235° C.

From the alcohol used to wash the crystals of trinitro mesitylene a small crop of barrel-shaped crystals was obtained which on repeated recrystallization gave a melting point of 167°, and contained 16.31 per cent of nitrogen. The theoretical nitrogen content of trinitro-trimethyl benzenes is 16.47 per cent, but the melting point is far too low for trinitro pseudocumene. The amount of this compound was too small for further experiments, and it remained unidentified.

NAPHTHALENE

Inspection of the distillation curve for the third series shows that the most decided rise in the whole curve appears between 215° and 235°, indicating a relatively large proportion of naphthalene. An attempt was made to estimate the amount of naphthalene in water gas tar as follows: 500 grams of tar were distilled to 260° C. and the naphthalene separating in the distillate

[1] Jour. Soc. Chem. Ind., 4, 78.
[2] Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 202.
[3] Ber., 10, 1009.

filtered off and pressed in a screw press; the filtrate was placed in a freezing mixture and the new crop of naphthalene crystals similarly removed; this filtrate was distilled collecting a fraction from 185°–265°, which was cooled, filtered and the naphthalene pressed; the new filtrate was refractioned, taking a fraction 195°–235°, which was similarly deprived of its naphthalene and the new filtrate distilled, collecting a fraction 210°–225°, which yielded but a very small separation of naphthalene when placed in a freezing mixture; the total weight of the solids thus recovered amounted to 8.0 per cent of the tar.

Naphthalene was prepared from the solids pressed from the distillate obtained from water gas tar between 200° and 250°. These solids were distilled, rejecting the first and last 10 per cent, and the distillate treated with sulfuric acid containing a little dichromate. The product, after thorough washing with water, was pressed and distilled, giving a product boiling at 217° C. (uncorrected) and melting at 80°, which showed no discoloration with concentrated sulfuric acid and remained perfectly white after an exposure of four months to the light.

ANTHRACENE

The above described experimental work was carried out for the most part on that part of the water gas tar which distilled below 250° C. in the initial distillation. The residue above 250° C. was worked up in collaboration with Dr. F. L. Haigh of this laboratory.

Two methods of distilling this residue were tried; in one the distillation was carried out with heat alone, in the other steam was introduced into the still in considerable volume. In both types of distillation most of the fractions showed a separation of solid materials on cooling. These solids were removed, pressed and weighed and the anthracene in them determined according to the method proposed by Meister, Lucius and Bruning,[1] "with appendix." This method consists in converting the anthracene into anthraquinone by treatment with chromic acid in glacial acetic acid solution. The anthraquinone was further purified by solution in fuming sulfuric acid and recovery therefrom by dilution.

The results of the dry distillation were as follows:

Temperature °C.	Per cent of solids in fractions	Per cent anthracene in solids	Temperature °C.	Per cent of solids in fractions	Per cent anthracene in solids
–265	None	...	335–345	4.19	41.75
265–305	None	...	345–355	4.27	34.85
305–315	1.32	65.49	355–360	3.39	26.41
315–325	2.32	61.35	360–370	4.36	7.41
325–335	3.85	42.82	370–400	None	...

These results show the presence of 0.392 per cent of anthracene in the residue above 250°, equivalent to 0.29 per cent of the original tar.

The thermometer readings in the steam distillation were of little value; the fractions were accordingly cut at about each 250 cc. of oil distillate in distillations

[1] Allen, "Commercial Organic Analysis," 3rd Ed., Vol. II, Pt. II, p. 229.

of 5000 grams of the "Residue." The solids were determined and analyzed with the results given below:

Fraction	Volume Cc.	Wt. of solids in fractions	Per cent of anthracene in solids
1.	250	None	...
2.	260	None	...
3.	250	None	...
4.	260	1.2	58.20
5.	250	5.8	47.26
6.	260	11.0	46.83
7.	250	15.2	40.52
8.	250	14.4	43.76
9.	250	12.1	39.19
10.	250	5.4	21.73
11.	260	None	...
12.	250	None	...

In the steam distillation, therefore, 0.517 per cent of anthracene was recovered from the "Residue" above 250°, equivalent to 0.383 per cent of the original tar. There was clearly less decomposition when steam was used, since the pitch contained but 5.6 per cent of free carbon, whereas that from the dry distillation averaged 57 per cent. Practically all of the anthracene comes over under 360° in the dry distillation, and at that temperature little cracking has taken place, the pitch containing but 6.0 per cent free carbon. Above 360° an orange-colored, viscous, semi-solid material appears in the distillate and seems to be indicative of marked decomposition.

Fairly pure anthracene was prepared from the expressed solids by washing with gasoline, and subliming the residue. This anthracene melted at 207°–211° C. and when mixed with a sample of Kahlbaum's anthracene, the mixture melted at 208°–211°.

As a further test of the quality of the solids pressed from the high boiling distillates of water gas tar, 50 grams of these solids recovered from the distillate between 289° and 361° were oxidized with bichromate and sulfuric acid. The anthraquinone after purification was sublimed giving 18.2 grams of crystalline anthraquinone. Anthraquinone prepared in this way was converted into the sodium anthraquinone-monosulfonate which in turn was converted into alizarine. A beautiful orange-red crystalline preparation of alizarine was obtained on subliming the product. Under laboratory conditions the transformation of anthraquinone into alizarine is difficult, and the yields obtained correspondingly low. From about 20 grams of anthraquinone only about 7 grams of alizarine were obtained.

SUMMARY

A systematic fractional distillation of water gas tar shows that it possesses a general resemblance to coal tar in its hydrocarbon content although, of course, the bases, phenols, and free carbon of the latter are absent or nearly so. The small amounts of material in the distillates resisting the action of sulfuric acid indicate an absence of paraffin and naphthene hydrocarbons, and the marked variation in the capacity for halogen addition points to variable amounts of unsaturated linkings outside the benzene ring.

Benzene, toluene, the xylenes, mesitylene, naphthalene, and anthracene were shown to be present in substantial amounts. The preparation of the pure hydrocarbons and of commercial products could be effected by methods similar to those employed with coal tar, and without encountering special difficulties.

It would appear probable that water gas tar may offer a commercial source of supply for the various grades of benzol and solvent naphtha. Naphthalene could readily be produced, but there is no adequate demand, and it is likely that the present trade conditions would not warrant the production of anthracene.

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THE RADIOACTIVITY OF SOME TYPE SOILS OF THE UNITED STATES

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Strutt[1] first called attention to the radioactivity of igneous and sedimentary rocks. The average of his results on igneous rocks showed a radium content of 3.3×10^{-12} grams of radium per gram of rock. The radium content of the sedimentaries was somewhat less. Joly[2] has examined a large number of rocks for radium and thorium. His radium values are somewhat larger than those of Strutt and other workers. The average of a number of his thorium determinations indicates the presence of 1.58×10^{-5} grams of thorium per gram of rock. Fletcher,[3] working primarily with secondary rocks, has confirmed Joly's results and at the same time pointed out that, with the exception of the calcareous rocks, those of the same types have always very nearly the same radium content.

Although a considerable amount of work has been done on the radioactivity of rocks and minerals, very little has been attempted along this line with soils. A knowledge that the atmosphere was radioactive was naturally followed by an investigation of the activity of the underground air. Elster and Geitel, Bumstead, Blanc, Gadourian, Wilson, Ebert, Eve, Sanders, Satterly and others have contributed to our knowledge of this subject. Whereas a study of the underground air indicates very plainly that the soil is radioactive, it does not give any absolute values for the activity of the soil itself, as the activity of the underground air depends as much upon the emanating power of the radioactive matter in the soil as it does upon the amount of that material actually present. Some rough minimum determinations have been attempted. Wilson states that there is probably seven times as much thorium as uranium in the surface soils at Manchester. Blanc, on the other hand, estimates that from 5 per cent to 70 per cent of the activity of the Roman soil is due to thorium; while Sanderson's[4] work indicates that 1 cc. of soil at New Haven produces radium emanation in equilibrium with 8.9×10^{-14} grams of radium, and thorium emanation in equilibrium with 1.35×10^{-8} grams of thorium. Fletcher[5] gives the radium content

[1] Proc. Roy. Soc., (A) **77** (1906), 472.
[2] Phil. Mag., **17** (1909), 760; **18** (1909), 140; **23** (1912), 201.
[3] Ibid., **23** (1912), 279.
[4] Am. Jour. Sci., **32** (1911), 169.
[5] Phil. Mag., **23** (1912), 279.

of two Dublin soils passing a 50-mesh sieve as 5.2×10^{-12} grams and 2.8×10^{-12} grams per gram of soil.

Strutt[1] states that the radium content of the Cambridge Gault is 1×10^{-12} grams per gram of material.

Satterly[2] measured the amount of radium emanation in the air of different soils at different intervals extending over a year. For depths of from 100–150 cm. in gravelly soil the amount of emanation is on the average 200×10^{-12} curies per liter. This is about 2,000 times as much as is usually in the atmosphere. He found that a liter of soil air was in association with 1200 grams of dry or 1400 grams of damp soil, and calculated from this that the apparent radium content of the soil is 1.7×10^{-14} grams per gram of dry soil. As the actual radium content of the soil is certainly very much larger than this, it follows that only a small portion of the emanation generated in the soil escapes under normal conditions from the soil particles into the air surrounding them.

Satterly also measured the proportion of radium emanation to thorium emanation in soil air at various depths. He found that the ratio increased from 1600 near the surface to 26,000 at a depth of 400 cm. At 150 cm. it is 8,600 and taking the radium content of the soil at 1.1×10^{-12} grams per gram of soil, he calculated that the thorium content would be 1.4×10^{-5} grams per gram of soil.

Apparently no systematic attempt has yet been made to correlate the radioactivity of soils with their other properties. Recently an elaborate study of the chemical composition of a number of type soils of the United States has been undertaken by G. H. Failyer and W. O. Robinson, of the U. S. Bureau of Soils. A mineralogical examination has been made of the same soils by Professor W. J. McCaughey. The author has these unpublished results at his disposal and has examined the soils for their radium content. The present paper constitutes a report on the results obtained.

Since radium is found in varying amounts in all rocks, spring waters, and even in underground waters, it is not surprising that botanists have tried the effects of the radium rays on the germination of seeds and the growth of plants. Since radioactivity is a factor of plant environment, it is possibly an agent in plant growth. Not only must the direct effect of the rays themselves be considered, but the chemical action induced by these rays, slight rises of temperature, etc., must be taken into account. The emanation, or gas, given off by radium salts diffuses through the soil, is dissolved by the soil solution, and comes in intimate contact with the plant roots even though the radium itself is in the soil as an insoluble sulfate or silicate. It is therefore more probable that if the presence of radium in the soil does affect the growth of plants appreciably, this effect will be more directly due to the influence of the emanation than to the radium. Some experimenters have not taken this fact into account and the influence of the β and γ rays on plants has in many cases been tested rather than bringing the roots in contact with the diluted emanation.

A far more serious objection to the experimental work with plants is that much greater amounts of radium have been employed than are ever present in the soil naturally, or likely to be added in actual agricultural or greenhouse practice. The amount normally present in soils is sensibly the same, namely, about 3 milligrams per acre foot. To increase this content one milligram per acre foot *in the form of ground ore* would cost about 20 dollars, and as pure radium salt about 120 dollars. The experimental work so far done indicates that at least several milligrams per acre would have to be added to produce an appreciable effect on the crop. Nevertheless, it seems well to call specific attention to some of the more important investigations in this direction.

Danysz[1] found that the rays from radium and the emanation hindered all species of bacteria in their development, some varieties being more sensitive than others.

Dixon[2] stated that the growth of cress seedlings was retarded by the β and γ rays from radium salts. Dixon and Wigham also found that β rays exercised an inhibitory action on the growth of certain bacilli.

Germination of the spores of *Aspergillus niger*[3] was found by Koernicke to be inhibited by exposure to the β and γ rays. Generally speaking, he found that roots were more sensitive than shoots.

Hussakof,[4] in a review published in 1907, showed that up to the time of his publication there was a general agreement on the following conclusions:

(1) The rays from radium affect the life processes of plants as well as animals. The Roentgen rays have a similar effect.

(2) Different species of plants are affected differently in degree.

(3) Younger tissues are more sensitive than older ones.

(4) The general effect is to retard all activity. There are a few exceptions.

(5) The growth and activity of enzymes are affected by the rays from radium.

Gager[5] found that in general the germination of both dry and wet seeds was retarded by the radium rays. Timothy grass seeds exposed to radium of weak activity showed an initial slowing up and then after five days an increased metabolism over the control culture. A similar result was obtained with bean seeds.

On the other hand, when unsoaked oat grains were planted at distances of 7, 22, and 45 mm. from a sealed glass tube containing 10 mg. radium bromide of 1,500,000 activity inserted in the soil, germination and subsequent growth were accelerated. The seeds farthest from the radium were accelerated most; those nearest, least. When timothy grass was grown in an atmosphere containing radium emanation, the result was dependent upon the amount of emanation used, the height above the soil at which the emanation was delivered, etc. Gager sums up by stating that "the

[1] *Proc. Roy. Soc.*, (A) **78** (1906–07).
[2] *Proc. Camb. Phil. Soc.*, **16**, p. 6.

[1] *Compt. Rend. Acad. Sci. Paris*, **136** (1903), 461.
[1] *Nature*, **69** (1903), 5.
[3] *Ber. deut. Bot. Ges.*, **22** (1904), 155.
[4] *Med. Record*, **72**, July 20, 1907.
[5] *Memoirs New York Botanical Gardens*, **4** (1908).

rays of radium act as a stimulus to protoplasm. Retardation of growth following an exposure to the rays is an expression of overstimulation. Acceleration of growth indicates stimulation between a minimum and an optimum point.''

Fabre[1] also studied the effect of radium emanation in the air on the germination of seeds and the growth of plants. The spores of *Sterigmatocystis nigra* on gelatin showed a retarded growth when exposed to strong doses of the emanation, the retardation being very largely proportionate to the amount of emanation. With *Linum catharticum* the germination of the seeds and the development of the plants were increased by increasing doses up to 1.5 microcuries per two liters of air. Above this, growth was retarded. It required a larger amount of emanation to retard germination. There seemed to be, however, an appreciable increase in the number of leaves developed on plants subjected to radium rays.

Acqua[2] gives the results of the effect of radium rays on the germination of seeds, development of seedlings, growth of pollen tubes and movements of protoplasm in several green plants. Great differences in reaction to the rays existed between different species and even between different organs of the same species. The root system generally responded when a more or less complete arrest of development was shown, although there were many exceptions. The aerial parts proved highly resistant, showing no general response either in stems or foliage. The pollen gave diverse results, some not growing at all, while others gave no reaction to the rays. Protoplasmic movements seem to be totally unaffected.

RADIUM CONTENT OF THE SOILS

All samples of soil used in this investigation were obtained by putting through a sieve of six meshes to the linear inch and grinding to an impalpable powder. Strutt's[3] method of getting the material in solution was used. The soil was fused with four times its weight of mixed alkali carbonates, treated with water, filtered, the residue washed with sodium carbonate solution to prevent hydrolysis, and then dissolved in hydrochloric acid. After standing a month, the combined emanation from the alkaline and acid solutions was introduced into the electroscope, which was of the C. T. R. Wilson type, modified by Boltwood.[4]

The standard used is that suggested by Boltwood.[5] It depends upon the fact that in old uranium minerals, the radium present bears a constant ratio to the uranium content of the mineral. Expressed in figures, 1 gram of uranium is in radioactive equilibrium with 3.3×10^{-7} grams of radium. Therefore, if the percentage of uranium in such a mineral is known, the amount of radium present is also known, and the emanation obtained from this radium can be used for standardizing the electroscope providing a correction is made for the amount of emanation which naturally

escapes at ordinary temperatures from the particular sample of mineral used. This must be determined for every sample of uranium mineral used for standardization.

McCoy[1] and Boltwood[2] showed that the ratio of radium to uranium in primary minerals, such as pitchblende, was constant. Their results were confirmed by Marckwald and Russell.[3] Mlle. Gleditsch,[4] however, obtained different ratios for different samples of pitchblende and following this there was a tendency to use dilute solutions of a pure radium salt as a standard. From such solutions, however, a portion of the radium nearly always precipitates sooner or later even though barium chloride is added. Heimann and Marckwald[5] have recently taken the matter up again and obtained the same ratio of radium to uranium in eight samples of pitchblende from different parts of the world, the average error being less than 0.5 per cent. It seems to be preferable, therefore, to use an analyzed pitchblende as a standard rather than a solution containing a radium salt.

The apparatus used for boiling off the emanation from the pitchblende for standardizing, and from the solutions obtained from the soils, was that designed by Schlundt and Moore.[6] All of the well known designs of apparatus for this purpose have been tested and compared by Randall,[7] who finds that the two forms of apparatus used by Schlundt and Moore give the highest ionization currents and the more uniform results.

Joly[8] has criticized the radioactive results obtained by the present method of getting rocks and minerals in solution. He claims that it is almost impossible to get solutions perfectly limpid and the precipitated silica carries down with it some of the radium. Although this is true to some extent, fairly concordant results can be obtained in the case of rocks and minerals by its use. Much more difficulty is experienced with soils than with rocks. Hydrolysis nearly always takes place and the filtering process is both long and tedious. On standing a short time silica invariably separated from the solutions. This was filtered off and fused again with alkali carbonates, and the process repeated until clear solutions were obtained. Even with the greatest care, some of the solutions became turbid before the emanation was boiled off. In order to lessen the difficulty with the silica, some of the soils were first treated with hydrofluoric and a little sulfuric acid. After evaporation and ignition, they were fused with fusion mixture in the ordinary way. The addition of the sulfuric acid at first sight would seem to be inadvisable, but as the solutions obtained by this method remained more limpid, and as practically all soils contain both sulfates and barium, it was thought that the advantages would outweigh the disadvantages. The

[1] *Compt. Rend. Soc. Biol.*, **70**, 187; **69**, 523; **70**, 419.
[2] *Ann. Bot. Rome*, [2] **8** (1910), 223–238.
[3] *Proc. Roy. Soc.*, (A) **77** (1906), 472.
[4] *Am. Jour. Sci.*, 4th Ser., **18** (1904), 97.
[5] *Ibid.*, **18** (1904), 381.

[1] *Ber. der deut. chem. Gesell.*, **36** (1903), 3093; *Jour. Am. Chem. Soc.*, **27** (1905), 391.
[2] *Phil. Mag.*, **9** (1905), 599.
[3] *Ber. der deut. chem. Gesell.*, **44** (1911), 771.
[4] *Le Radium*, **8** (1911), 256.
[5] *Jahrb. Rad. u. Elektron.*, **10** (1913), 299; *Phys. Zeit.*, **14** (1913), 303.
[6] *Jour. Phys. Chem.*, **9** (1905), 320.
[7] *Trans. Am. Electrochem. Soc.*, **21** (1912).
[8] *Phil. Mag.*, **22** (1911), 134.

results obtained, however, seemed to be low, so duplicate samples of the soils treated in this manner were fused in the ordinary way and a comparison of the results is given in Table I. In column B the results are given when the soil was treated with hydrofluoric and sulfuric acids previous to fusion. Column A gives the results when these acids were not used.

TABLE I

NO.		DEPTH	RADIUM (Gram $\times$ 10^{-12} per gram of soil)	
			A	B
1	Volusa silt loam, Naples, N. Y.........	0″–8″	0.93	3.76
2	Volusa silt loam, Naples, N. Y.........	8″–36″	1.10	..
3	Cecil clay, Charlotte, N. C............	0″–6″	1.94	0.54
4	Cecil clay, Charlotte, N. C............	6″–36″	0.78	..
5	Cecil sandy loam, Charlotte, N. C.....	0″–8″	1.26	0.28
6	Cecil sandy loam, Charlotte, N. C.....	8″–36″	1.95	1.33
7	Durham sandy loam, Ancher, N. C.....	0″–10″	1.73	0.45
8	Durham sandy loam, Ancher, N. C.....	10″–36″	1.66	..
9	Norfolk sandy loam, Laurinburg, N. C..	0″–14″	2.56	..
10	Norfolk sandy loam, Laurinburg, N. C..	14″–36″	2.80	..
11	Decatur clay loam, Hollywood, Ala....	0″–4″	2.78	..
12	Decatur clay loam, Hollywood, Ala....	4″–36″	1.52	1.27
13	Hagerstown loam......................	0″–8″	2.57	1.21
14	Hagerstown loam......................	8″–36″	0.83	1.13

When the activity was determined both with the use of sulfuric and hydrofluoric acids, and without, the results in six of the eight cases were uniformly lower when sulfuric acid was used. In the case of the Volusa silt loam soil, which is an exception, the results are so much at variance with the others that a suspicion as to the reliability of the figure 3.76 $\times$ 10^{-12} at once arose. An examination of the records showed the possibility, though not the certainty, of a contamination of this solution owing to an accident. This possibility of contamination, however, should cause the above figure to be rejected. In the case of the Hagerstown loam the two values are close, but there is no explanation for the discrepancy with the other results. A preliminary report on this work[1] was made before the two methods were used on the same samples. This preliminary report, therefore, does not show the variations in the results obtained.

In four cases, as shown in Table II, the soil is more active than the subsoil; in three, the reverse is true. The average activity of the soils is 1.97 $\times$ 10^{-12}, and that of the subsoils is 1.52 $\times$ 10^{-12}.

There seems to be a fairly definite relationship between the activity and the combined amounts of barium and strontium. In the majority of cases the soil or subsoil which has the highest activity also has the largest amount of barium plus strontium. The Hagerstown loam and Decatur clay loam are exceptions, the soil of the latter having a considerably larger activity than the subsoil, but carries a little less barium and strontium. The same reaction holds fairly well with the amount of sulfur present. In the Cecil clay and Durham sandy loam the amount of sulfur in the soil and subsoil in each case is the same, although the activity of the soil is greater. In only one case, however, the Decatur clay loam again, are the figures actually reversed.

This relationship between the activity of the soil

and the amount of barium, strontium and sulfur present is not surprising. Since radium has an insoluble sulfate, which precipitates with the sulfates of barium and strontium, the above results seem to indicate that radium in the soil is very largely, if not entirely, in the form of sulfate.

The number of samples tested does not justify any attempt to correlate the activities of the different soils with their productivity. Such figures would be reliable only when a much larger number of results are available.

The amount of rare earths present in the soils as determined by Failyer and Robinson[1] was so small that no conclusion can be drawn by a comparison of the rare earth content with the amount of activity.

TABLE II

SOIL	ACTIVITY Gram $\times$ 10^{-12} per gram of material		BaO(a) and SrO(a)		SULFUR(a)	
	Soil	Subsoil	Soil	Subsoil	Soil	Subsoil
Cecil clay..................	1.94	0.78	0.10	0.05	0.07	0.07
Durham sandy loam.........	1.73	1.66	0.16	0.14	0.06	0.06
Decatur clay loam..........	2.78	1.52	0.06	0.07	0.13	0.19
Hagerstown loam...........	2.57	0.83	0.17	0.17	0.39	0.14
Volusa silt loam............	0.93	1.10	0.08	0.10	0.09	0.10
Cecil sandy loam...........	1.26	1.95	0.05	0.05	0.04	0.09
Norfolk sandy loam.........	2.56	2.80	0.02	0.03	0.07	0.13
	13.77	10.64	0.64	0.61	0.85	0.78
Average...................	1.97	1.52	0.09	0.09	0.12	0.11

(a) Unpublished determinations by Failyer and Robinson.

Since the activity of at least secondary rocks of the same type is fairly constant, it would seem that there ought to be more connection between the mineralogical composition of a soil and its activity. Unfortunately, the mineralogical data at my disposal are not sufficiently complete to draw any such connection. Only the potash feldspars and micas were determined quantitatively—the others qualitatively, and as most rock-forming minerals occur in all soils, the qualitative results showed no significance. Monazite occurs in some soils, but was not specially looked for in the twelve samples examined and was not listed among the minerals in any of them.

THORIUM CONTENT OF THE SOILS

After experimenting with other methods,[2] that used by Joly for determining the thorium of rocks and minerals was finally decided on. Fig. I shows the apparatus. A is the flask containing the solution of the material to be tested. In this case it contained either the acid or alkaline solution obtained from fusion of the soil with fusion mixture. B is a drying tube containing at one end calcium chloride and at the other, phosphorus pentoxide, the two separated by a plug of glass wool. C is a tube of small diameter, with a bulb at the top and dipping at the bottom into a fairly heavy oil. D is the electroscope and at E there is a needle valve (not shown).

The flask A is first disconnected from the apparatus and the solution boiled vigorously for ten minutes. This is to get rid of the radium emanation. Thorium emanation is boiled off, of course, at the same time,

but as the half-life period of the radium emanation is 4.8 days and that of the thorium emanation 54 seconds, the latter is very rapidly and the former very slowly reformed. Hence any active gas which is found in the solution after the ten minutes' boiling and during the progress of the experiment can be considered as thorium and not radium emanation.

The flask A is now connected with B and gently boiled while a constant current of air is drawn through the whole apparatus in the direction of the electroscope. This current can be controlled by the needle valve. C assists in regulating the pressure in the apparatus. If the boiling is steady the leaf does not vibrate and readings are readily made.

If the air is pulled too rapidly through the apparatus, the emanation is too much diluted; if too slowly, a considerable portion of the emanation decays before it reaches the electroscope. A maximum effect can therefore only be obtained by trial.

The activity of any given soil is, of course, the sum of the activities of the acid and alkaline solutions obtained from that soil.

The natural leak of the electroscope under the experimental conditions is obtained by substituting for A, a similar flask containing distilled water and boiling as already described. It was noted that if air was
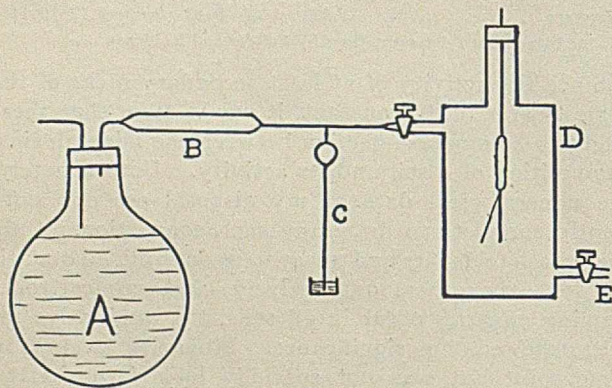

Fig. I

passed over calcium chloride and phosphorus pentoxide and then through the electroscope, the leak was smaller than when no air was passed. Also, if the leaf was steady and air was then passed, the leaf slowly rose during a period of ten minutes and usually over about five small scale divisions. This result is probably closely connected with the observations made by Schlundt and Moore[1] in a somewhat similar case, and discussed by Randall[2] in a later paper. Readings were made only after the maximum point was reached.

The electroscope was standardized by using an acid solution of a thorium mineral in which the disintegration products are in equilibrium. In the present case an analyzed specimen of thorianite was used. A flask containing distilled water, to which a certain volume of the standard thorianite solution was added, was substituted for A after first boiling to get rid of the radium emanation. The effect on the electroscope of the emanation from a known quantity of thorium

[1] *Trans. Am. Electrochem. Soc.*, **8** (1905), 292.
[2] *Ibid.*, **21** (1912), 463.

could therefore be observed and compared with the results obtained from the soil solutions under similar conditions after the leak was deducted in each case.

In order to test the accuracy of the method, different thorianite solutions of known strength were used and the results compared. For example, 10 cc. containing 0.0021 gram thorium metal gave (leak deducted) a drop of twelve divisions per hour. 40 cc. of the same solutions gave a drop of 47.8 divisions per hour.

The results obtained are shown in Table III.

TABLE III

	Depth	Thorium gram $\times 10^{-5}$ per gram of soil
Durham sandy loam	10″–36″	5.4
Norfolk sandy loam	0″–14″	3.3
Decatur clay loam	4″–36″	5.6
Hagerstown loam	8″–36″	4.02
York silt loam	0″–8″	4.37

The results are not numerous enough to justify any conclusions as regards the relative amounts of thorium in the soils and subsoils. Comparing them with Joly's results on rocks, they seem to indicate that soils contain more thorium than most rocks, the average of the above results being much higher than the average of Joly's results, viz., 1.58×10^{-5} gram per gram of rock. The figures are also higher than those obtained by Blanc for Roman soils.[1]

Strutt[2] has shown that the amount of radium in the earth's crust is more than sufficient to account for its internal heat. He did not take into account the thorium present. Averaging the amount of radium in the soils and subsoils and reducing this back to the uranium content, it can readily be seen that the amount of uranium present is about 10 per cent that of the thorium. While it is difficult to state just to what extent the thorium assists in maintaining the earth's internal heat, the effect must at least be appreciable.

The small variation in the amount of thorium in the five samples tested is noteworthy.

My thanks are due to Dr. Frank K. Cameron, Chief of the Division of Physical and Chemical Investigations, Bureau of Soils, for many courtesies extended during the progress of this investigation.

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PARTIAL AND INTERMITTENT COMBUSTION OF GAS

By E. E. SOMERMEIER

COMBUSTIBLE, INFLAMMABLE AND EXPLOSIVE MIXTURES

A *combustible mixture* is usually defined as a mixture of a composition such that if any part of it is raised to its ignition temperature a reaction between the components will become self-sustaining and will extend to all parts of the mixture; an *inflammable mixture* as a mixture of a composition such that if it is ignited at any point a visible flame will spread throughout the entire mixture; an *explosive mixture* as a mixture of a composition such that if a portion of it is raised to its ignition temperature an explosive reaction will

[1] *Phil. Mag.*, **18** (1909), 146–148.
[2] *Proc. Roy. Soc.*, (A) **77** (1906), 472–485.

take place throughout the entire mass. Given a sufficiently large volume of gas any mixture which is combustible or inflammable is also explosive.

With the combustion once started any one of three things is possible: The reaction may decrease in rapidity; it may remain constant; or it may increase in rapidity. An exactly constant rate of reaction is so rare that it may be disregarded as a possibility and the reaction may be expected either to accelerate or to decrease in velocity. If it accelerates an explosion will occur, provided a sufficiently large volume of gas is present. If it decreases, the combustion will die out and the gas, practically speaking, will be incombustible or at least only partially combustible.

DATA ON THE COMPOSITION OF COMBUSTIBLE AND EXPLOSIVE MIXTURES

The data in the literature regarding the lower limits of combustible and explosive mixtures of gas with air or with oxygen differ greatly. As an illustration, Hempel[1] gives the lower limit of combustible mixtures of hydrogen with air as from 5 to 6 per cent. Most other authorities give from 9 to 10 per cent. Techlu[2] gives the lower limits of an explosive mixture of methane with air as 3.2 per cent. Burrell[3] gives 5.5 per cent. Most other authorities give about 6.0 per cent. In comparing such widely different values one is at a loss as to the real facts. That differences of such magnitude are due to errors of manipulations on the part of some of the experimenters is hardly probable and they are rather to be ascribed to differences in conditions and in methods of work.

Some of the more probable factors contributing to these differences in experimental results are: (1) Impurities in the gases with which the experiments were performed. (2) Differences in the initial temperature of the gas. (3) Differences in the initial pressure of the gas. (4) Differences in the volumes of gas used. (5) Differences in method of ignition. (6) Differences in the design or style of the containers.

The recorded results, unless otherwise noted, were presumably obtained by starting at ordinary laboratory temperature and at atmospheric pressure, and it is hardly possible that any large amounts of unknown impurities were present in the gas mixtures used. It would therefore appear that no great discrepancies in results are to be explained by any or all of the first three sources of error, and large variations are more probably to be explained as due to the latter three. By varying these conditions the writer, as will be shown later in this paper, obtained results, which, while they are not entirely concordant, do tend to suggest reasons for the different values given for combustible and explosive mixtures.

EXPERIMENTS TO TEST THE INFLUENCE OF VOLUME OF GAS, METHOD OF IGNITION AND STYLE OF CONTAINER

In the experiments described in this paper the following volumes of gas mixtures were used:

[1] "Gas Analysis," Hempel.
[2] *J. prakt. Chem.*, **75** (1907), 212.
[3] THIS JOURNAL, **5** (1913), 181.

No.	CONTAINER Dimensions Diam. Cm.	Length Cm.	Kind	Vol. cc.	Condition of experiment
1......	..	..	Glass flask	145	Gas confined
2......	8	26	Iron cylinder	1,300	Gas confined
3......	9.5	29	Glass cylinder	2,100	Open at end
4......	20	38	Iron cylinder	13,000	Gas confined
5......	30	42	Iron cylinder	30,000	Gas confined

DIMENSIONS OF THE CONTAINERS—For the smallest container an ordinary short-neck globular CO_2 flask was used. This flask when stoppered had a capacity of 145 cc.

Each of the iron cylinders was fitted with an opening for the attachment of a water-sealed glass tube, with an opening for the insertion of a stopper carrying copper lead wires to which the wire fuses were attached and with two pet cocks or openings through which gas could be admitted or withdrawn and also through which water could be admitted to replace the gas withdrawn in sampling.

The accompanying cut of the 13,000 cc. cylinder shows the general arrangement of the stirring apparatus, glass delivery tube, paraffined paper-top, etc. The
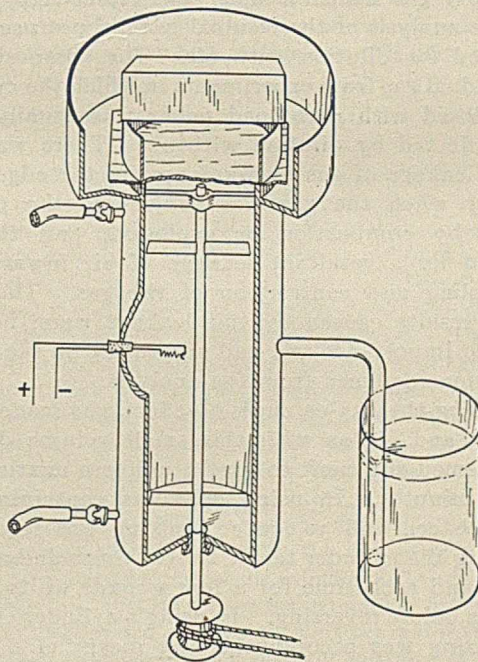
projecting flange at the top is of galvanized iron and was used when it was desired to secure a water seal around paraffined paper. In experiments with mixtures rich enough to produce much of a reaction several thicknesses of paraffined paper were used and the necessary weight to hold the paper in place secured by using the ring above the paper as the fulcrum of a lever 5 or 6 feet long, upon the end of which weights were placed. In this way pressures equivalent to 700 or 800 pounds upon the head of the cylinder were readily secured.

The following methods of ignition were used:

1   0.5 to 0.75 cm. No. 34 platinum wire, heated to white heat.
2   0.5 and 5 cm. No. 34 platinum wire, fused.
3   0.5 and 5 cm. No. 34 iron wire, fused.
4   5 cm. No. 34 tantalum wire, fused.
5   0.25 cm. spark from induction coil.
6   Oxygen-natural gas flame.

In performing the experiments with closed containers, two methods of observing whether or not a reaction took place were used.

(1) A bent glass tube was attached to the container, the open end of which dipped into water. With a vigorous reaction, gas was forced through the tube and bubbled up through the water. With a less vigorous reaction, the water in the tube was depressed through a noticeable distance.

DIAMETERS OF DELIVERY TUBES USED

| 145 cc. flask | 3 mm. tube | 13,000 cc. cylinder | 12 mm. tube |
| 1,300 cc. cylinder | 6 mm. tube | 30,000 cc. cylinder | 12 mm. tube |

(2) The mouth of the container was closed with paraffined paper, which, being flexible, was visibly moved by a slight reaction in the gas mixture, while with a vigorous explosion or combustion it was ruptured. This method was employed in some of the experiments with the cylinders of capacities of 1300 cc. and 13,000 cc.

In the experiments in which a delivery tube was used, any gas which escaped was replaced by water, and the analysis of the residual gas did not need to be corrected for dilution with air. The composition of the residual gas from experiments in which the cylinders were closed with paraffined paper was usually somewhat affected by dilution with air. There was more or less leakage of gas outward around the edge of the cylinder when the gas was subject to the pressure caused by combustion or explosion, and this was followed by a resultant leakage of air inward upon the cooling and contraction of the gas. The errors in the results caused by this leakage were, however, of minor importance and had no bearing on the general conclusions deduced from the analysis.

In using the 145 cc. flask no effort was made to mix the gas and air, as with this small volume diffusion was deemed sufficient to give a uniform mixture after a few minutes. In using cylinders containing 1300 cc., 2000 cc., and 30,000 cc., mixing was secured by inverting the cylinder ten or twelve times and allowing it to stand each time for a few seconds up to several minutes before reversing. In using a cylinder of 13,000 cc., mixing was accomplished by means of a pair of fan blades on a rotating shaft which was turned several hundred times before the ignition of the mixture.

The current used for heating the 0.5 to 0.75 cm. of No. 34 platinum wire to a white heat was obtained by using two 32 candle power carbon lamps in parallel. For fusing the platinum, iron and tantalum wires, three to four 32 candle power lamps in parallel were used. In the fusing of the platinum wire less than one calorie of heat was developed. In the fusion of the iron and tantalum wires slightly more heat may have been developed owing to some oxidation. In the experiments with the 13,000 cc. cylinder one calorie of heat would be sufficient to raise the temperature of the gas mixture only about 3° C.

All the experiments were performed at laboratory temperatures which varied for different days from as low as 18° C. to as high as 27° C. Some of the results obtained with the different methods of ignition and the different volumes of gas together with analyses of the resultant gases are as follows:

HYDROGEN AND AIR

WITH THE 145 CC. FLASK—Method of ignition, 0.5 cm. No. 34 platinum wire heated to white heat for 2 seconds. A blank on air under the same conditions gave a 5 cm. depression of water in the delivery tube.

RESULTS WITH DIFFERENT PERCENTAGES OF HYDROGEN IN AIR

Per cent hydrogen	Depression Cm.	Per cent hydrogen	Depression Cm.
4.5	10	6.0	20
5.0	15	7.1	70
5.5	20	8.2	Flask blown off of the stopper.

Turning on the current for two additional intervals of one second each gave further reactions as follows:

Per cent hydrogen	Depressions Cm.	Per cent hydrogen	Depressions Cm.
5.0	15 and 10	6.0	20 and 12
5.5	20 and 10	7.1	20 and 15

After the third ignition of the 5.5 per cent mixture, analysis of residual gas for oxygen showed that only 0.2 per cent of the oxygen had burned, equivalent to 0.4 per cent of hydrogen.

RESULTS WITH A 0.25 CM. SPARK FOR 0.5 SEC. FROM AN INDUCTION COIL

Per cent hydrogen	Depression Cm.	Per cent hydrogen	Depression Cm.
4.3		5.6	
1st spark........	20	1st spark.......	25
2nd spark.......	20	2nd spark.......	25
3rd spark.......	5	7.0	
		1st spark.......	75
		2nd spark.......	50

WITH THE 1300 CC. CYLINDER—Method of ignition, fusion of 0.75 cm. of No. 34 iron wire. Extent of reaction noted by movement of paraffined paper on the head of the cylinder.

Per cent hydrogen	Result	Per cent hydrogen	Result
4.5	No visible reaction	7	Very fair reaction
4.6	Very faint reaction	8	Weak explosion
5.0	Fair reaction	9	Fair explosion, not violent
6.0	Fair reaction	10	Vigorous explosion

WITH THE CYLINDER WATER-SEALED, glass tube to allow the escape of gas, and an iron wire fuse, several experiments with 7.7 per cent hydrogen all gave vigorous reactions, gas being forced out through the water-seal. Analysis of the residual gas for oxygen showed that from 1.4 to 2 per cent of hydrogen had burned.

WITH THE 13,000 CC. CYLINDER, iron wire fuse and 6 per cent hydrogen, about 500 cc. of the gas were forced out through 20 cm. of water. An analysis of the residual gas for oxygen showed that about 0.5 per cent of hydrogen had burned. With 7.7 per cent hydrogen about 2 liters of gas were forced out of the cylinder. An analysis of the residual gas showed that 0.4 per cent hydrogen had burned. Ignition of the residual gas by means of additional fuses gave combustion reactions up to 10 fuses. Up to the fourth fuse the reaction produced forced gas out of the cylinder through 30 cm. of water. Using 0.5 cm. of No. 34 platinum wire heated to a white heat for two seconds, a 7.7 per cent mixture of hydrogen gave two distinct reactions, the gas escaping through 20 cm. of water in two closely succeeding but distinctly separate portions. Analysis of the residual gas showed that 1.6 per cent of hydrogen had burned.

Using a spark from the induction coil for about 0.1 second, a 7.7 per cent mixture of hydrogen gave a very vigorous reaction, several liters of gas being forced out of the cylinders. Analysis of the residual gas indicated that 0.8 per cent of hydrogen had burned. With 7.6 per cent hydrogen and with the spark left running for several seconds, three distinct reactions were observed.

WITH THE 30,000 CC. CYLINDER and iron wire fuse, mixtures of from 7.3 to 7.7 per cent hydrogen gave fair reactions as was indicated by the forcing of gas out of the cylinder through water. Analysis of the residual gas showed that only about 0.4 per cent of hydrogen had burned. A 7.7 per cent mixture ignited with a dozen successive fuses gave reactions each time; up to the ninth fuse, the reaction forced gas out of the cylinder through 18 cm. of water; whereas, the burning of a fuse in the cylinder filled with air gave no visible depression.

NATURAL GAS AND AIR

Natural gas from the Columbus, Ohio, city mains was used. This gas on analysis was found to consist of approximately 85 per cent of methane and 15 per cent of ethane.

WITH THE 145 CC. FLASK, a 5 per cent mixture of natural gas and air gave no visible reaction when ignited with 0.75 cm. of No. 34 platinum wire heated to a white heat.

Per cent natural gas in air	Spark	Time of spark Seconds	Depression Cm.	Per cent natural gas in air	Spark	Time of spark Seconds	Depression Cm.
4.4	1st	1	30	5.6	1st	1/2	75
	2nd	1	20		2nd	2	60
	3rd	1	20		3rd	2	50
5.0	1st	1	30		4th	4	75
	2nd	1	25	Blank on air	1st	1	10
					2nd	5	20

On several other tests with mixtures containing from 5.7 per cent to 5.2 per cent of gas and using a spark for 0.5 second, the flask was blown from the stopper.

WITH THE 1300 CC. CYLINDER—Method of ignition, fusion of from 0.5 to 0.75 cm. No. 34 platinum or iron wire. A 4.6 per cent mixture of gas and air produced a 4 cm. depression. A blank on air produced a depression of 1 cm.

A mixture of 4.8 per cent of gas and air produced vigorous reactions, gas being forced out against a pressure of 5 lbs. per square inch. Analysis showed the presence of 2.6 per cent CO_2, indicating that about one-half of the gas had been burned. With paraffined paper closing one end of the cylinder, and with a 0.75 cm. platinum wire heated to fusion, a fair reaction was detected with as low as 4.6 to 4.7 per cent mixtures of natural gas and air. Mixtures of from 4.9 to 5 per cent of gas and air gave fair combustion, a distinct flame being visible.

RESULTS WITH 5 CM. NO. 34 IRON AND PLATINUM FUSES—Blanks on fuses in air gave for the iron fuse a depression of 12 cm. and for the platinum fuse a depression of 10 cm. A 4.3 per cent mixture of gas and air gave a depression of 30 cm. with an iron fuse and a depression of 20 cm. with a platinum fuse. Using a 5 cm. tantalum wire fuse, blanks on fuse in air gave a depression of 12 cm. Mixtures of 4.3 per cent and 4.4 per cent of gas and air gave depressions of 40 and 50 cm., respectively.

WITH THE 13,000 CC. CYLINDER, iron wire fuse, paraffined paper head on cylinder.

With a 4.7 per cent mixture of natural gas, no visible reaction was produced.

With a 4.8 per cent mixture of natural gas, a faint reaction was produced.

With a 5 per cent mixture of natural gas, a fair reaction was produced.

With a 5.2 to 5.3 per cent mixture of natural gas, a fair reaction was produced, the paper head of the cylinder being scorched by the heat of the combustion.

Tests after combustion on the residual gas from mixtures containing 5.2 and 5.3 per cent of natural gas gave results for CO_2 of from 0.8 to 1.2 per cent, indicating that approximately this amount of the natural gas had burned. These values are, however, somewhat too low, owing to the leaks inward of air after combustion. This is shown by the more complete analysis after combustion of the residual gas from a 5 per cent mixture of natural gas, upon which values were obtained as follows: CO_2 1.4, CH_4 2.7, C_2H_6 0.6 per cent.

On the basis of natural gas consisting of approximately 85 per cent CH_4 and 15 per cent C_2H_6 the original mixture contained 4.25 per cent of CH_4 and 0.75 per cent of C_2H_6. On the residual gas after combustion the C_2H_6 is 0.15 per cent lower and the CH_4 1.55 per cent lower than in the original mixture. If these amounts burned to CO_2 the CO_2 formed would equal $1.55 + 0.30 = 1.85$ per cent as against 1.4 per cent of CO_2 actually found. This corresponds to a dilution of the original mixture with approximately 25 per cent of air.

EFFECT ON IGNITION BY A WHITE HOT PLATINUM WIRE COMPARED WITH IGNITION BY FUSION OF THE WIRE

A 5.1 per cent mixture with 0.75 cm. No. 34 platinum wire heated to a white heat for two seconds gave no visible reaction, but upon turning on additional current and fusing the wire, a fair reaction occurred, about 500 cc. of gas being forced out of the cylinder. Analysis of the residual gas for carbon dioxide and oxygen indicated that only about 0.2 per cent of the natural gas had burned.

The ignition of the gas by fusion of the wire and its failure to ignite from the wire raised to a white heat shows very clearly the great effect of a very high temperature of ignition upon the starting of the reaction.

EXPERIMENTS WITH THE OXYGEN-NATURAL GAS FLAME AS A SOURCE OF IGNITION

Mixtures of natural gas and air, and hydrogen and air were collected over water in the 2100 cc. glass cylinder which was then closed with a glass plate. The gases were mixed by inverting the cylinder a number of times, and then with the cylinder inverted, it was quickly slipped off the glass plate which closed it and passed over the oxygen gas flame, the flame being in the cylinder for about one-half second. This flame was about 10 cm. long and consumed about 3 cc. of natural gas per second. With natural gas no visible combustion was obtained with 5 per cent of gas, but with a 5.5 per cent mixture the combustion was quite evident, a blue flame spreading slowly throughout the cylinder. With hydrogen no reaction was detected with a 6 per cent mixture. With a 7 per cent and a 7.7 per cent mixture no visible flame was noticeable but an appreciable reaction was indicated by the deposit of a film of moisture upon the cold sides of the cylinder. That an appreciable reaction is started by the oxygen-natural gas flame in mixtures of natural gas and air lower than 5.5 per cent is shown by the following experiments upon different mixtures of gas and air in the 13,000 cc. cylinder: In making the experiments a cork was removed from a 2 cm. opening in the side of the cylinder and the tip of the flame inserted into the cylinder for from 1 to 3 seconds. Considerable reaction occurred as was shown by the rapid swelling of the paraffined paper top used to close the cylinder and by the rapid escape of gas through the opening in which the flame was inserted. In each case the effect was greater than that which was produced in blank tests upon the cylinder filled with air. But in the mixtures used no violent reaction occurred. The extent of the reaction was approximately determined by analysis of the residual mixtures for CO_2. The flame used 3 cc. of natural gas, and produced approximately 3 cc. of CO_2 per second; or in the 13,000 cc. mixture less than 0.03 per cent of CO_2 per second was added from this source. The results obtained upon the residual mixtures were as follows:

Per cent of natural gas in mixture	Time of flame in cylinder Seconds	Per cent CO₂ in resultant mixture	CO₂ from flame	Per cent of CO₂ from gas burned	Approxi- mate cc. of natural gas burned
4.4	5	1.0	0.15	0.85	100
4.0	5	1.0	0.15	0.85	100
3.2	3	0.6	0.10	0.50	60
2.0	4	0.3	0.10	0.20	25

These results all show appreciable combustion around the flame. This combustion was in all cases greater than is shown by these results on account of the expansion of the gas and the dilution of the remaining gas with air upon contraction before the gas was sampled and analyzed. That partial combustion of such mixtures occurs is shown by the well known lengthening of a lamp flame in air containing fire damp.

ANALYSIS OF RESULTS

The experiments here recorded show conclusively that with a high initial ignition temperature a reaction may start in a gas mixture, which, as a whole, may be incombustible because the heat of combustion is not sufficient to maintain the temperature at the kindling point. Hence all of the mixture will not burn although the reaction may be sufficiently extensive as to make the mixture appear to be combustible or explosive. With the source of high temperature employed to cause ignition acting for only a very brief interval of time, as during the fusion of platinum or iron wire, the resultant reaction quickly ceases but not until a combustion of gas has occurred, the heat of which is in some cases equivalent to hundreds of time the energy required to heat the platinum or iron fuse. The heat liberated by the fusion of 0.75 cm. of No. 34 platinum or iron wire is only a fraction of a calorie. In a 7.7 per cent mixture of hydrogen this fuse, as has been shown, causes a combustion of 0.4 per cent of hydrogen in a 30,000 cc. mixture or of 120 cc. of hydrogen. This liberates about 300 calories of heat. In the smaller containers a greater percentage of the hydrogen was burned. For example, in the 1300 cc. cylinder as high as 2 per cent of hydrogen burned or only 26 cc. From this it would appear that when the combustion is started from a source of very high temperature, more gas is burned in a large volume of mixture than in a small volume, but that the greater percentage of the gas is burned in the smaller mixture. This is at least partially accounted for by the cooling of the gas by the walls of the container, especially where small volumes are burned; but with large volumes of gas, as in the case of the two large cylinders holding 13,000 and 30,000 cc., respectively, this would be of little effect, and in a room full of gas the effect would be entirely negligible. With a continuous source of high temperature, as with a white hot wire, a lamp flame or a running electric spark, the reaction produced may be intermittent. The gas immediately around the point of ignition burns and expands, and combustion around that point ceases until another portion of the mixture of gas and air has replaced the expanded gas and products of combustion, whereupon another reaction takes place resulting in a series of combustions or explosions.

The limits of appreciable ignition or combustion of hydrogen and of natural gas in air vary with the volume of gas used, the source of ignition and the style of the container. In a 2000 cc. open cylinder the lower limit obtained for natural gas is about 5.5 per cent. With hydrogen the lower limit for very appreciable ignition was above 7 per cent. In a closed container the lower limit for natural gas using 0.5 cm. of No. 34 platinum wire heated white hot, was over 5 per cent. With a 0.5 cm. platinum or iron wire fused the lower limit obtained was 4.7 to 4.8 per cent. With a 5 cm. No. 34 wire fused the lower limit obtained was about 4.3 per cent. With a 5 cm. No. 36 tantalum wire fused the lower limit was about 4.3 per cent. With a 0.25 cm. spark from an induction coil the lower limit of appreciable reaction was about 4.3 per cent. With closed containers, 6 to 7 per cent mixtures of hydrogen and air gave vigorous reactions with 0.5 cm. platinum or iron wire fuses. With the electric spark, mixtures as low as 5 per cent gave very noticeable reactions, and faint reactions were obtained with mixtures as low as 4.3 to 4.6 per cent.

For the same percentage of gas and the same method of ignition, small volumes of gas gave more vigorous reactions than large volumes, but in total amount of gas burned, the combustion obtained in large volumes was greater than that obtained in small volumes.

With smaller containers, or with a more powerful spark, or a longer wire fuse, undoubtedly very appreciable reactions can be obtained with mixtures of lower percentages than those given, but with ordinary sources of ignition, large volumes of gas will not react appreciably unless the mixture is richer in gas than the lowest limits obtained in these experiments. However, the thermal calculations[1] based on 850° and 700° as the ignition temperature required for explosive mixtures of natural gas and of hydrogen with air indicate that mixtures of natural gas in excess of 2 per cent and of hydrogen in excess of 5.9 per cent are potentially explosive if conditions favorable to the reaction are present. Some of these conditions, in addition to a vigorous source of ignition, are unusually high in initial temperature of the mixtures of gas and air, presence of fine combustible dust, and an increase in the pressure of the mixture.

The results of these experiments indicate that a comparatively small excess of hydrogen above the theoretical requirement is necessary to produce a vigorous reaction. Natural gas or methane, on the other hand, ignites with such difficulty that, with ordinary methods of ignition, an appreciable reaction does not occur unless a very large excess of gas is present above that required by the thermal calculation.

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WOOD DISTILLATION UNDER DIMINISHED PRESSURE A CONTRIBUTION TO THE PROBLEM OF UTILIZATION OF WOOD WASTE

By MAXWELL ADAMS AND CHARLES HILTON

The rapid decrease in the supply of long leaf pine available for the production of turpentine and the immense waste of resinous wood in the lumber indus-

[1] THIS JOURNAL, 6, 191.

try throughout the country has stimulated chemists in an effort to devise some practical method for the extraction of wood turpentine from stumps, lapwood and mill waste. According to the Report of the Bureau of Chemistry[1] there are more than five million cords of waste wood left annually in the forests in the lumbering of resinous woods. The amount of waste is greatly increased when we add to this the dead and fallen timber of the uncut forest.

The methods for extracting turpentine from resinous wood, so far proposed, may be classed under four heads: 1. Destructive distillation, with or without steam. 2. Steam distillation. 3. Distillation with hot rosin. 4. Extraction with volatile solvents. These methods have all been tried out with varying degrees of success, but it is somewhat doubtful if any of them have developed beyond the experimental stage. The commercial success of any method will depend largely upon the demand for the by-products, and the utilization of all parts of the wood. The steam distillation process in conjunction with the manufacture of paper pulp appears promising[2] and the destructive distillation method has often been successful where charcoal, creosote and rosin oils are in demand.

The method described in this paper proposes to improve the ordinary destructive distillation process by controlling the temperature and diminishing the pressure at which the distillation takes place, thereby avoiding superheating and at the same time vaporizing the turpentine at a temperature below which it will not decompose.

According to Violette,[3] when wood is carefully heated to 150° C. water only is distilled, and decomposition begins at about 160° C. These results will probably vary with the kind of wood. In order to determine the effect of heat upon the variety of wood to be used in later experiments a sample of western yellow pine, *Pinus ponderosa*, was placed in a flask immersed in a sulfuric acid bath and heated very slowly. Care was taken that the temperature of the bath did not exceed that of the interior of the flask by more than five degrees. At 94° (the barometric pressure of the laboratory being 645 mm.) distillation of water and turpentine begins. When kept at 160° C. for several hours the wood turns brown, and above this temperature there is abundant evidence of decomposition. Gaseous decomposition begins when a temperature of 220° C. is reached.

Although pure turpentine distils at 155–6°, yet when dry wood is heated only a small percentage of the turpentine present is driven off when decomposition begins. This is explained by the fact that ordinary pitch as it occurs in wood is a solution of rosin and various waxes in turpentine; when a substance is dissolved in a liquid, the vapor pressure of the solvent is lowered at all temperatures, and the solution must therefore be heated to a higher temperature than would be required for the pure solvent, before distillation begins.

[1] *Bull.* **159**.
[2] Bur. of Chem., *Bull.* **159**.
[3] Sadtler's "Industrial Organic Chemistry," p. 348.

The rosin is not volatile; as the turpentine distils and the solution grows more concentrated, the vapor pressure is lowered, and the boiling point is correspondingly raised, until the temperature of decomposition is reached, and a large part of the turpentine is destroyed before it is vaporized. The presence of water in the wood, however, adds a factor which partly counterbalances this, and lowers the boiling point
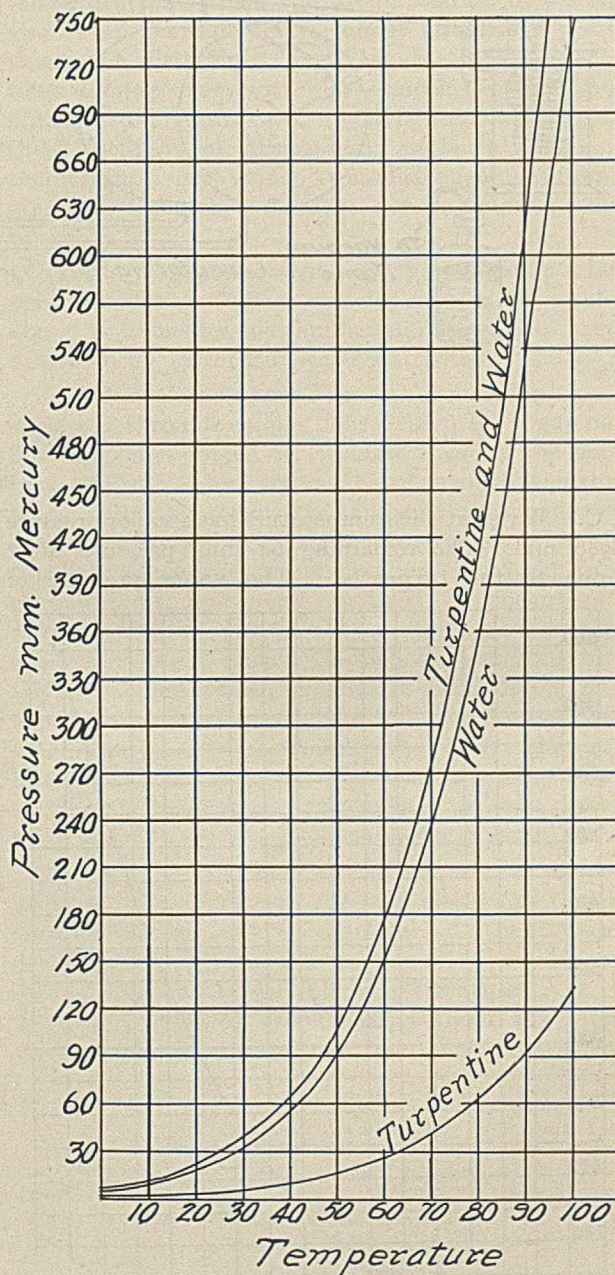
FIG. 1.

of the turpentine in the mixture. According to the law of Regnault[1] for immiscible liquids, water and turpentine will distil at the temperature at which the sum of their vapor pressures is greater than atmospheric pressure, neither influencing the vapor pressure of the other. The quantity of each liquid found in the distillate will be proportional to their vapor densi-

[1] *Pogg. Ann.*, **93**, 537.

ties and can be calculated by means of Avogadro's law.

A mixture of water and turpentine (the barometric pressure in the laboratory being 652 mm.) boils at

If we consider the gram molecular volume at 93° as being $\dfrac{22.4\,(273+93)}{273}$ liters, and assume turpentine to consist of pinene with a molecular weight of 136,
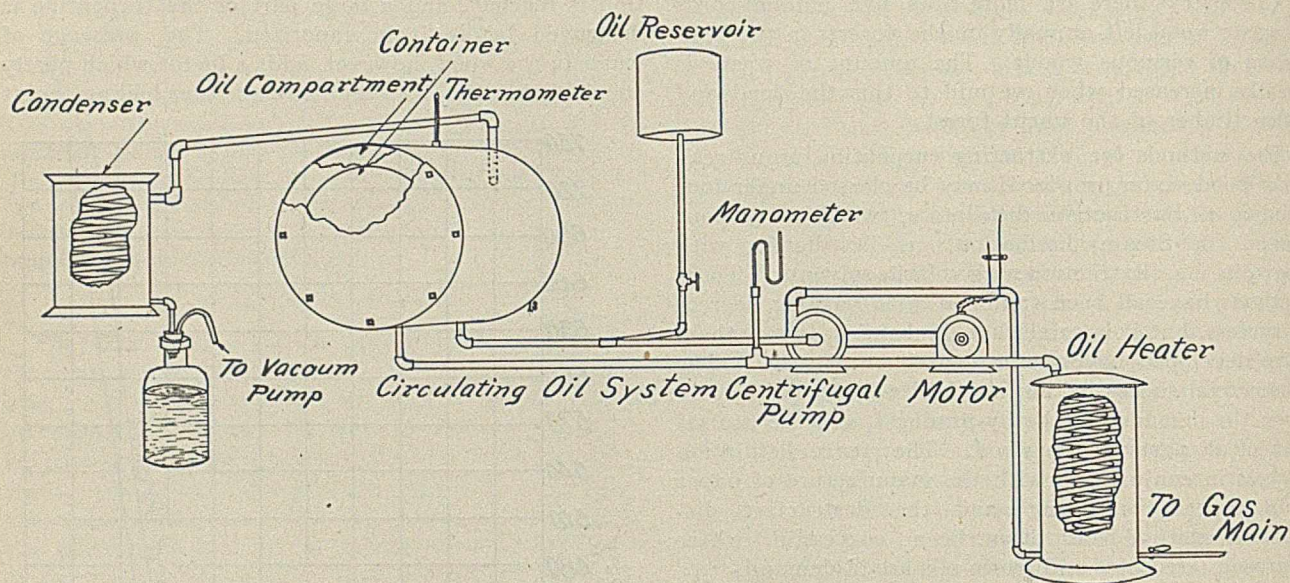
FIG. 2

93° C. Water at this temperature has a vapor pressure of 588 mm. The remaining 64 mm. pressure must be due to the turpentine. The vapor pressure of

then the mixed vapors will be found to consist of $\dfrac{18 \times 588}{652} = 16.2$ parts of water vapor and $\dfrac{136 \times 64}{652} = 13.3$ parts of turpentine vapor. The ratio of the weight of water to turpentine in the vapor is approximately 100 to 80, and this is also the ratio of their weights in the distillate.

The density of turpentine is 0.85, therefore the volume of water and the volume of turpentine are practically equal when the distillation takes place at atmospheric pressure, but the proportion of turpentine in the distillate should be considerably increased when the distillation is carried on under diminished pressure, as is shown by the examination of the vapor pressure curves in Fig. 1.

The vapor pressure of turpentine at 30° is 6.9 mm. and that of water at the same temperature is 31.5 mm.; a total of 38.4 mm. By applying the preceding method of calculation we find that the mixed vapors at 30° will consist of $\dfrac{18 \times 31.5}{38.4} = 14.7$ parts of water vapor and $\dfrac{136 \times 6.9}{38.4} = 24.4$ parts of turpentine vapor. Thus the amount of turpentine vaporized is practically double that of the water, when the distillation takes place at 38 mm. pressure. These results are confirmed by experiment.

FIG. 3

pure turpentine[1] shows that a mixture of it and water should boil at about 91° C. The slight solubility of each in the other doubtless lowers the vapor tension of both.

[1] "Smithsonian Physical Tables," p. 126.

When we apply the steam distillation method to the extraction of turpentine from wood, the proportion of turpentine is very much diminished, and the distillation temperature is considerably higher, due to the presence of dissolved resins, which have greatly diminished the vapor pressure of the turpentine. Experiments show that, under the most favorable conditions, 15 parts of water remove 1 part of turpentine. The proportion of water, however, varies

widely, depending upon the rate of distillation and the size of the wood chips.

TABLE I

Number of fraction	Temp. of oil bath °C.	Temp. of dist. flask °C.	Expt. No. 1 Press. normal		Expt. No. 2 Press. 35 mm.	
			Vol. turp. Cc.	Vol. water Cc.	Vol. turp. Cc.	Vol. water Cc.
A.............	100–150	40– 94	0.0	0.0	7.2	3.1
B.............	150–190	94–120	5.3	4.2	2.8	2.2
C.............	190–200	120–140	4.3	3.2	2.5	1.9
D.............	200–220	140–160	1.4	0.6	1.1	1.5
E.............	220–270	160–180	1.8	1.6	2.1	3.0
F.............	270–300	180–200	2.3	4.0	4.6	3.2
G.............	300–330	200–220	3.1	6.1	6.4	4.1

By decreasing the pressure, according to the preceding theoretical considerations, the amount of the turpentine produced at a given temperature should be

TABLE II

Frac.	Dist. temp. °C.	Expt. No. 3, press. normal			Expt. No. 4, press. 80 cm.		
		Vol. crude turp. Cc.	Sp. gr. crude turp.	Vol. refined turp. Cc.	Vol. crude turp. Cc.	Sp. gr. crude turp.	Vol. refined turp. Cc.
A....	Up to 220	570	0.855	501	920	0.887	722
B....	220–250	220	0.884	176	320	0.934	182

considerably increased. Accordingly, an ordinary distilling apparatus, with a capacity of about 200 grams of wood shavings, was fitted up and attached to a

TABLE III

Variety of wood used	Frac.	Temp. of distil. °C.	Time of distil.	Vol. of refined turp. obt. at ord. press. Cc.	Vol. of refined turp. obt. at 80 cm. press. Cc.
Pinus Monophylla...	A	Up to 220	1 hr 30 m.	180	250
Pinus Monophylla...	B	220–250	1 hr.	108	150
Pinus Jefryii........	A	Up to 200	1 and ½ hr.	100	150
Pinus Jefryii........	B	200–220	1 hr.	95	105
Pinus Jefryii........	C	220–250	1 hr.	80	75

pump capable of maintaining the apparatus at a pressure of 35 mm. To avoid superheating, the distilling flask was placed in an oil bath. A sample of thoroughly dry, western yellow pine, fairly rich in pitch, was cut into chips, which would pass through

represent the extremes of variation. Time being an important factor in determining the quantity of distillate obtained from wood, the temperature was raised 20° in approximately 30 minutes. Time and temperature thus being the same in both experiments, the variation in the amount of distillate secured in the different fractions must depend upon the pressure. The distillate coming over below 160°, the temperature at which the decomposition of wood begins is 20 per cent greater under diminished pressure than that distilling at ordinary pressure. The fractions coming over, both above and below 160°, under diminished pressure are much lighter in color than those distilling at atmospheric pressure. When the temperature reaches 220° gaseous decomposition begins and diminished pressure can no longer be maintained.

In order to repeat the above experiments on a larger scale, a double-walled retort, capable of holding about 25 kilos of wood, and similar in form to the one described by Pritchard[1] was constructed.

The plan of the apparatus is shown in Fig. 2. Oil is passed through copper coils heated in a gas flame. The hot oil is forced to circulate through the outside jacket of the retort by means of a small centrifugal pump. By this means the temperature is under complete control and superheating is avoided. The door, through which the retort is filled, is closed with a ground joint, and made air-tight by means of set screws. The vapors from the retort pass through a condenser into a receiver, which is connected with a Geryk vacuum pump, capable of maintaining the entire apparatus, when in operation, at a pressure of 80 cm. The oil used to conduct the heat to the retort has a flash point of over 300° C. and is capable of withstanding a temperature of 400° C. without cracking, when heated in a closed vessel under pressure.

To test the efficiency of the method, a sample of western yellow pine was cut into pieces one foot long and about one inch in diameter, thoroughly dried, divided into three equal portions of 22 kilos each, and subjected to the following treatment: I. Distilled in a retort by direct heat, without any attempt at temperature control or fractional separation of

TABLE IV

No. of fraction	Temperature of retort °C.	Vol. in cc. of pyro. acid obtained	Sp. gr. of pyro. acid	Per cent wood alcohol in pyro. acid	Per cent acetic acid in pyro. acid	Vol. in cc. of tar obtained	Sp. gr. of tar	Per cent tar distilling			Per cent pitch residue in flask	Per cent water in tar
								below 180° C.	between 180°–240°	between 240°–320°		
A..........	160–200	1275	1.002	0.49	0.64	835	0.855	83.5	3.0	2.1	9.6	1.8
B..........	200–240	560	1.013	0.91	1.13	280	0.884	62.5	4.2	5.0	27.2	2.1
C..........	240–270	885	1.041	1.43	4.01	590	0.930	39.6	12.8	14.6	31.1	1.9
D..........	270–280	675	1.053	1.65	5.06	420	0.953	25.2	16.9	19.2	35.8	2.9
E..........	280–290	1045	1.061	2.15	5.48	925	0.993	13.9	12.5	16.3	44.7	2.8
F..........	290–300	975	1.070	3.68	4.54	1000	1.025	10.1	12.2	14.3	61.4	2.0
G..........	300–360	920	1.073	2.67	2.65	960	1.032	7.4	11.2	13.8	65.3	2.3

a half inch mesh. The sample was thoroughly mixed and 175 grams were used in each experiment, the results of which are given in Table I.

On account of the difficulties of heat control there was some variation in the oil bath temperatures of Experiments 1 and 2. The numbers in Column 2

the crude distillate. II. Distilled in an oil-jacketed retort under atmospheric pressure. III. Distilled in an oil-jacketed retort under a pressure of 80 cm.

Method No. I yielded 1606 cc. of tar from which was extracted 424 cc. of a light brown, ill smelling,

[1] THIS JOURNAL, 4, 338.

TABLE V

Variety of wood used in the distillation	Vol. of pyroligneous acid in liters	Per cent wood alcohol in pyro. acid	Per cent acetic acid in pyro. acid	Vol. of tar in liters	Per cent turpentine oil in tar	Per cent creosote oil in tar	Per cent mixed heavy oil in tar	Per cent pitch in tar	Per cent water in tar	Kilos of charcoal
Sugar pine............	9.8	0.52	2.6	1.26	8.5	9.0	15.7	56.1	10.2	3.64
Yellow pine.........	12.4	0.55	2.2	2.09	10.6	6.2	20.2	46.9	6.5	4.32
Stump wood-pine....	10.9	0.57	2.4	3.50	18.1	9.0	20.4	50.4	2.4	4.09
Red fir	11.1	0.48	1.8	1.78	16.1	7.8	18.4	47.1	11.2	5.03
Silver fir	10.1	0.51	2.1	1.23	11.2	11.0	18.4	53.1	8.4	4.77
Mill states..........	9.6	0.61	2.7	1.81	9.2	8.1	20.7	48.8	11.8	4.53
Sage brush..........	9.4	3.54	11.53	1.94	...	16.2	14.7	15.6	48.0	7.8

wood turpentine, distilling below 170°. The results obtained from Experiments 3 and 4 are given in Table II.

Sample A is almost colorless and easily purified by distillation, but Sample B contains impurities, which can be removed only by alternately washing with caustic soda and sulfuric acid and redistilling.

Experiments 3 and 4 were repeated, using samples of other kinds of wood with results given in Table III.

From the above results it is evident that the yield of turpentine under diminished pressure is from 10 to 20 per cent higher than that obtained at ordinary pressure, using the same method of heat control, while it is double that obtained by the common destructive distillation method. In addition to this the quality of the product is much improved. If, however, as shown by a number of experiments in this laboratory, the wood used is green, and contains water in large excess of the volume of turpentine, then the process becomes one of steam distillation and the diminished pressure, while bringing the distillate over at a lower temperature, produces no decided increase in the total yield of turpentine.

The samples of purified wood turpentine, obtained from each of these varieties of wood, is water white and looks like ordinary spirits of turpentine, but they differ from it, and from each other, in odor and optical properties. They are under examination in this laboratory in an effort to identify the various terpenes present.

When the temperature of the retort reaches 250°, the volume of the gases given off is so great that the pump is no longer efficient in reducing the pressure, and distillation under diminished pressure becomes impossible. In order, however, to determine the total amount and the properties of the different products obtained at various temperatures from western yellow pine, 22 kilos of a sample of dry "light wood" were submitted to distillation in an oil-jacketed retort with results tabulated in Table IV.

After the distillation there remained 7.8 kilos of charcoal. The time for the distillation of each fraction was one and a half hours and the temperature was raised at almost uniform rate.

There are many varieties of wood indigenous to the Pacific coast, concerning the distillation products of which there is no published data. Samples of a number of these varieties, as they occur in the lumber districts of the Sierra Nevada Mountains, were submitted to destructive distillation. The results obtained are set down in Table V. The amount of wood used in each experiment was 25 kilos, and the methods used in the examination of the distillate are those described in Allen's "Commercial Organic Analysis."

SUMMARY

The above experiments show that:

I. The western conifers contain wood turpentine in commercial quantities.

II. Under favorable conditions a cord (4,000 lbs.) of yellow pine will yield 25 gallons of wood turpentine.

III. The yield of turpentine from a given sample of dry wood can be increased by distilling under diminished pressure.

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THE NATURE OF BASIC LEAD CARBONATE

By EDWIN EUSTON
Received February 24, 1914

In an article[1] "On the Composition of White Lead," reasons were presented for the assertion that white lead consists of a mixture of normal lead carbonate with a basic carbonate of lead of the composition $PbCO_3.Pb(OH)_2$. The purpose of the present paper is to consider the nature of the combination of the components of this basic carbonate of lead. The existing assumption in text books on pigments is that, in basic carbonate of lead, the lead carbonate and the lead hydroxide are firmly united in actual chemical combination, but the results obtained in the experiments here to be mentioned indicate rather that the basic carbonate of lead should be considered as among those substances described by Zsigmondy[2] as mixtures of colloidal substances which can, under certain conditions, act as chemical compounds. "Not only[3] have colloid compounds or colloidal mixtures, in which two colloids are united, been erroneously described as chemical compounds, but so also have mixtures or adsorption compounds of crystalloids with colloids."

The fact that the lead hydroxide portion of basic lead carbonate is soluble in ammonium chloride solution but not in cane sugar solution, indicates that the lead hydroxide is not present in mere mechanical mixture and yet is not so firmly held as to be properly considered in chemical combination. Direct evidence that the basic carbonate of lead is an "adsorption compound" is afforded by the fact that, in more than fifty trials, various samples of white lead and of lead carbonate, when treated with basic lead acetate solution at room temperature by stirring or agitation, invariably withdrew lead hydroxide from the solution and correspond-

[1] THIS JOURNAL, March, 1914.
[2] "Colloids and the Ultramicroscope," N. Y., 1909, p. 68.
[3] Ibid., p. 69.

ingly gained in weight. In composition the samples before treatment ranged from 12.0 to 16.3 per cent CO_2, and after treatment contained as low as 10.1 and 10.3 per cent CO_2 in extreme cases. The extent of the reaction under uniform temperature conditions is dependent on the basicity of the lead acetate solution, on the relative amounts of the sample to be treated and of the available lead hydroxide in the solution, and on the duration of the treatment. Merely enough agitation is required to ensure uniform treatment. The process proceeds slowly, requiring, for example, six hours in one instance to enable a sample containing 14.7 per cent CO_2 to join with enough lead hydroxide from the solution to reduce to 10.1 per cent CO_2 in the final product. Excess of basic lead acetate in solution beyond the calculated amount is required for complete action, as the end point of the reaction is an equilibrium determined by the relative basicity of the solution and of the sample under treatment. With a sample containing both normal lead carbonate and basic lead carbonate this equilibrium can be disturbed in either direction at will by the addition of a further quantity of basic lead acetate solution or by the addition of neutral lead acetate solution. Samples prepared from lead carbonate in the manner described respond to the tests for basic lead carbonate to the extent that their analyses indicate.

To learn whether normal lead carbonate is unique in its ability to withdraw lead hydroxide from basic lead acetate solution, similar trials, using considerable excess of basic lead acetate solution, were then made with kaolin, commercial zinc oxide, basic zinc carbonate, whiting, precipitated calcium carbonate, precipitated barium sulfate and precipitated barium carbonate. The kaolin gained 10.6 per cent in weight by addition of lead hydroxide, and two different brands of zinc oxide gained only 0.6 per cent each. The other substances named formed compounds corresponding approximately to the following formulae:

Basic zinc carbonate became $ZnCO_3.Zn(OH)_2.3Pb(OH)_2$.

Whiting became $2CaCO_3.Pb(OH)_2$.

Precipitated $CaCO_3$ became $2CaCO_3.Pb(OH)_2$.

Precipitated $BaSO_4$ became $3BaSO_4.Pb(OH)_2$.

Precipitated $BaCO_3$ became $3BaCO_3.2Pb(OH)_2$.

The calcium compounds and the barium sulfate compound were so lacking in opacity as to be worthless as pigments. The barium carbonate compound and the basic zinc carbonate compound showed marked improvement in density, in opacity, in brushing quality, and in rapidity of drying with linseed oil, in these respects closely resembling white lead. In tinting and spreading power the basic zinc carbonate compound equalled white lead, and the barium carbonate compound considerably exceeded it. These results show that other substances than normal lead carbonate form compounds with lead hydroxide from basic lead acetate solution, and that the lead hydroxide so combined tends to give to such compounds, in varying degree, characteristics as pigments heretofore ascribed only to white lead. Further similarity is shown by the lead hydroxide portion of the compounds being soluble in

ammonium chloride solution but not in cane sugar solution.

The slow withdrawal of lead hydroxide from basic lead acetate solution by normal lead carbonate to form basic lead carbonate, the like action of some other substances in forming lead hydroxide compounds, the similarity in some properties conferred by the lead hydroxide on these different compounds, and the fact that the lead hydroxide is present neither in mechanical mixture nor in true chemical combination, indicate that basic lead carbonate is an adsorption compound.

EUSTON WHITE LEAD COMPANY, ST. LOUIS

THERMAL REACTIONS IN CARBURETING WATER GAS
PART I—THEORETICAL

By M. C. WHITAKER AND W. F. RITTMAN

Much careful scientific work has been done on the equilibria involved in the manufacture of uncarbureted blue water gas. In the combined processes of manufacturing and carbureting blue water gas according to present practice, few experiments have been made on the equilibria of the constituents to find out the effect of varying pressure, temperature and concentration conditions. In the technical literature of gas manufacture, one rarely finds a reference to the relationship which may exist between the spheres of reaction in the process. The natural conclusion has been that the water gas and oil gas reactions are separate and influence each other but little.

It is proposed to consider some of the factors in which the H_2, CO, CO_2 and H_2O of the blue water gas may affect the proportions of CH_4, C_2H_6, C_2H_4, H_2, etc., resulting from the cracking of the gas oil which is added. Likewise the influence of the gases coming from the oil on the percentage composition of the final gas mixture will be considered.

When the blue water gas or oil gas are manufactured in separate operations, hydrogen is the only gas which is found in the free state, in any quantity. But if the two gases, separately made, should be brought together at high temperature in a container such as a gas plant superheater, would there not be new equilibria to be satisfied? For example, might not the CO and H_2 of one become CH_4 and H_2O of the other, or *vice versa?* In case of these new equilibria there would, of course, be vital reactions between the gases of the two processes. In actual manufacturing practice, all the gases produced are in intimate contact at high temperature for the greater part of the manufacturing period, *i. e.*, while passing through the carbureter and superheater. Is it then correct to regard carbureted water gas as the result of two distinct reactions?

Equilibrium conditions tend to establish themselves both during the periods of initial cracking of the oil and the subsequent passage of the mixture through the carbureter and superheater. Gas oil itself can be "cracked" in a short distance, as has been shown in practically all laboratory experiments; in the laboratory the length of the cracking tube is usually a question of inches. It would seem on *a priori* grounds that the only important reason for the existence of the superheater is to enable the various

gases present to interact ("fix") and reach a favorable equilibrium.

This laboratory has begun a comprehensive study of the reactions and equilibria involved in water gas manufacture. While unable to cover the field in two years, it has come to a full realization of the importance of the investigation. The present paper will be confined to a theoretical consideration of the problem. Further papers will take up experimental data.

The problem has been attacked entirely from the point of view of physical chemistry, and from the standpoint of mass action and thermodynamics. In so doing, the mechanism of the reactions involved has not been seriously considered. The materials at the start, the final products desired, the energy transformations essential to bring the latter from the former, the temperature, the pressure and the concentration conditions favorable to the changes have had primary consideration.

Basing an experimental investigation upon the theoretical considerations evolved, we have been able, among other things, to establish the following results:

(1) Increase the yield of illuminants over the best results recorded in the literature by more than 100 per cent.

(2) Decrease the carbon deposited to less than 1 per cent, by weight, of the oil used.

(3) Make an oil gas in which 56 per cent of the fixed gases are illuminants.

These figures result from the application of conditions more favorable to the theoretical deductions than at present used in water gas manufacture. Conversely by applying conditions more unfavorable to the theory involved, and comparing the maximum yield under these conditions with a maximum yield obtained under ordinary conditions, it has been found possible to:

(4) Decrease the yield of illuminants by 25 per cent.

(5) Increase the carbon deposited to 51.5 per cent, by weight, of the oil used.

(6) Make an oil gas containing only 5 per cent total illuminants.

Further, it has been found possible to produce:

(7) A viscous tar of relatively high specific gravity containing naphthalene and anthracene; or

(8) A liquid "tar" of relatively low specific gravity resembling petroleum oil, and containing no naphthalene and anthracene.

In dealing with the problem, no single reaction can be considered exclusively by itself. All the reactions are vitally interrelated, though any single reaction, or set of reactions, may be extremely important as indicating a tendency. The experiments are designed to obtain the largest yield of hydrocarbons, and to eliminate, as much as possible, CO_2, water vapor, deposited carbon, and tar vapors. The goal is to increase the yield of illuminants.

MANUFACTURE OF UNCARBURETED BLUE WATER GAS

The manufacture of blue water gas may be represented by the equations:

$$C + H_2O = CO + H_2 - 29,300 \text{ cal.} \qquad (1)$$
$$C + 2H_2O = CO_2 + 2H_2 - 19,000 \text{ cal.} \qquad (2)$$
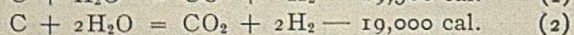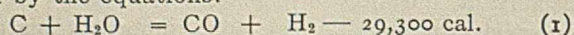
The two equations are combined by subtracting (2) from (1) in order to eliminate the carbon:

$$CO_2 + H_2 = CO + H_2O - 10,300 \text{ cal.}$$
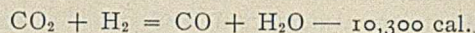
Equilibrium is established between these gases when

$$K = \frac{p_{CO}\, p_{H_2O}}{p_{CO_2}\, p_{H_2}}$$

where K represents the usual equilibrium constant; *i. e.*, the value of the product of the partial pressures of CO and H_2O divided by the product of the partial pressures of CO_2 and H_2. K has a definite value for each definite absolute temperature.

For a practical illustration of the significance of equilibrium conditions in the manufacture of blue water gas, assume a theoretically ideal mixture consisting of 50 per cent H_2 and 50 per cent CO. Pass the two gases through a chamber heated to 700° C. (1290° F.) until they reach the equilibrium of this temperature; what are the resulting gases? K at this temperature is in the neighborhood of 0.32.

$$3CO + H_2 = CO_2 + H_2O + 2C + 67750 \text{ cal.}$$
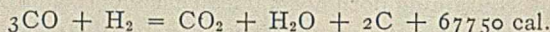
Under equilibrium conditions

Let X = volume CO_2
then X = volume H_2O
0.5 — X = volume H_2
0.5 — 3X = volume CO
∴ 1 — 2X = total final volume

$\dfrac{X}{1-2X}$ = partial pressure CO_2 $\dfrac{0.5-X}{1-2X}$ = partial pressure H_2

$\dfrac{X}{1-2X}$ = partial pressure H_2O $\dfrac{0.5-3X}{1-2X}$ = partial pressure CO

$$K = 0.32 = \frac{p_{CO_2}\, p_{H_2O}}{p^3_{CO}\, p_{H_2}} = \frac{\left(\dfrac{X}{1-2X}\right)\left(\dfrac{X}{1-2X}\right)}{\left(\dfrac{0.5-3X}{1-2X}\right)^3\left(\dfrac{0.5-X}{1-2X}\right)} = \frac{2X^2(1-2X)}{(0.5-3X)^2}$$

Solving, X = 0.069 = 6.9 per cent

2X = gas lost in reaction = 13.8 per cent

$\dfrac{X}{1-2X} = \dfrac{0.069}{0.862}$ = 8 per cent CO_2

$\dfrac{X}{1-2X} = \dfrac{0.069}{0.862}$ = 8 per cent H_2O

$\dfrac{0.5-3X}{1-2X} = \dfrac{0.293}{0.862}$ = 34 per cent CO

$\dfrac{5-X}{1-2X} = \dfrac{0.431}{0.862}$ = 50 per cent H_2

Applying the above calculations to a mixture of 1,000 cu. ft. each of carbon monoxide and hydrogen, and assuming that no hydrocarbons are formed, there would be a net loss of 13.8 per cent (276 cu. ft.) due to the reaction, leaving 1,724 cu. ft. of mixed gases, as follows:

1724 × 0.08 = 138 cu. ft. CO_2
1724 × 0.08 = 138 cu. ft. H_2O
1724 × 0.34 = 586 cu. ft. CO
1724 × 0.50 = 862 cu. ft. H_2

The water in condensing leaves a net volume of permanent gases equal to 1724 — 138 = 1586 cu. ft. This permanent gas is composed of 8.7 per cent CO_2, 37 per cent CO and 54.3 per cent H_2. There would be also a deposit of 9.25 pounds of carbon. In other words, there are only 1586 — 138 = *1448 cu. ft.* of the original H_2 and CO remaining.

Different temperature conditions would obviously give different results. A numerical problem of this nature shows how vitally equilibria conditions influence gas manufacture, and indicates the commercial importance of an understanding of such equilibria

conditions. Just as the equilibria conditions here are of importance, it can be shown that they are no less important when the reactions are between CO, H_2, CO_2, and H_2O coming from the blue water gas on one hand, and H_2, CH_4, C_2H_6, C_2H_4, and tar vapors, etc., coming from the gas oil on the other hand.

The blue water gas reactions and equilibria have been investigated[1] and are well understood, so that we know what conditions are favorable and what are unfavorable; i. e., degree of temperature, quantity of steam, depth of fuel bed, etc.

MANUFACTURE OF STRAIGHT OIL GAS

The manufacture of an oil gas as carried out by the Pintsch or Blau Gas companies is an old process, but is not as well understood as the blue water gas equilibrium. Few experimental equilibria of the various components of oil gas have been worked out, as have been the CO_2, CO, H_2O and H_2 relations of blue water gas. Here, one at once faces the fact that in the oil cracking process, instead of the four gases of the blue water gas reaction, there are all the members of the methane, ethylene and acetylene series, as well as those hydrocarbons which constitute the tars produced in pyrogenetic decomposition.

Synthetic methane has been made from carbon and hydrogen,[2] where equilibrium exists when
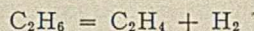
$$K = \frac{p_{CH_4}}{p^2_{H_2}}$$

Similarly, we may conclude that equilibrium exists between H_2 and all of the other hydrocarbons.

By combining the ethane and ethylene equations through the elimination of carbon, one gets $C_2H_6 = C_2H_4 + H_2$, where equilibrium conditions prevail when

$$K = \frac{p_{C_2H_4} \, p_{H_2}}{p_{C_2H_6}}$$

For a practical illustration of the meaning of this expression, assume a volume of C_2H_6 and heat it. Eliminating other reactions than the one between ethane and ethylene, consider the resultant relative quantities of H_2, C_2H_6 and C_2H_4 at a temperature of 900° C., taking the value of K equal to 1.26

$$C_2H_6 = C_2H_4 + H_2$$

Let X = volume H_2
then X = volume C_2H_4
$1 - X$ = volume C_2H_6
∴ $1 + X$ = total final volume

$\dfrac{X}{1+X}$ = partial pressure C_2H_4

$\dfrac{X}{1+X}$ = partial pressure H_2

$\dfrac{1-X}{1+X}$ = partial pressure C_2H_6

$$K = 1.26 = \frac{\left(\dfrac{X}{1+X}\right)\left(\dfrac{X}{1+X}\right)}{\left(\dfrac{1-X}{1+X}\right)} = \frac{X^2}{1-X^2}$$

Solving, $X = 0.74$

$\dfrac{0.74}{1.74} = 42.6$ per cent C_2H_4, $\dfrac{0.74}{1.74} = 42.6$ per cent H_2

and $\dfrac{0.26}{1.74} = 14.8$ per cent C_2H_6.

In dealing with any of these equilibria expressions, one must be careful to remember that no single equilibrium can be considered by itself. In the ethane–hydrogen–ethylene equilibrium at 900° C., for instance, there is a pronounced tendency for the ethane to go to ethylene; and in practice one should, therefore, expect a high ethylene yield, but by referring to the ethylene–benzene system one finds that at 900° C. there is an even greater tendency for the ethylene to be removed by polymerization to benzene. Assuming a volume of C_2H_4 and bringing it to equilibrium at 900° C., observe the resultant relative quantities of C_2H_4 and C_6H_6:

$$3C_2H_4 = C_6H_6 + 3H_2 + 32500 \text{ cal.}$$
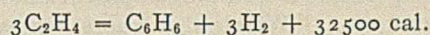
Under equilibrium conditions

X = volume C_6H_6
$3X$ = volume H_2
$1 - 3X$ = volume C_2H_4
∴ $1 + X$ = total final volume

$\dfrac{X}{1+X}$ = partial pressure of C_6H_6 $\dfrac{1-3X}{1+X}$ = partial pressure C_2H_4

$\dfrac{3X}{1+X}$ = partial pressure of H_2

$$K = \frac{p_{C_6H_6} \, p^3_{H_2}}{p^3_{C_2H_4}} = 68 \times 10^9 = \frac{\left(\dfrac{X}{1+X}\right)\left(\dfrac{3X}{1+X}\right)^3}{\left(\dfrac{1-3X}{1+X}\right)^3} = \frac{27X^4}{(1+X)(1-3X)^3}$$

Solving, $X = 0.33$

$\dfrac{0.33}{1.33} = 24.8$ per cent C_6H_6, $\dfrac{0.99}{1.33} = 74.4$ per cent H_2

and $\dfrac{0.01}{1.33} = 0.8$ per cent C_2H_4.

Thus an experimental test, using the first equilibrium without a consideration of the second, would result in disappointment. Further, not only must the ethane–hydrogen–ethylene–benzene equilibrium be satisfied, but each of these constituents must, in turn, be in equilibrium with methane, acetylene, propane, naphthalene, etc. In short, there will be a grand symphony of equilibria between all components of the system.

Equilibria expressions, such as the ones just given, are therefore of value when properly understood and used as a basis for experimental proof. First of all, the time element is very important to insure final equilibrium; and secondly, their mathematical derivations involve integration factors based on physical properties such as specific heat, vapor pressure, heat of reaction, etc., under conditions which have not been experimentally determined. Experimental demonstration based upon a few selected and isolated equilibria is almost certain to result in failure, due to overlooking other equally important equilibria which might modify or even reverse the direction of final reactions.

Sufficient experimental and commercial work has been done on the making of all oil gas under atmospheric conditions[1] to give empirical data indicating that as

[1] Bureau of Mines, Bulletin 7, 1911; Jüptner, Chem. Ztg., 1904, p. 902; K. Neuman, Stahl und Eisen, 1913, p. 394; O. Hahn, Z. physik. Chem., 44, 513–547; C. LeChatelier and K. Neuman, Stahl und Eisen, 1913, p. 1485; E. A. Allcut, Engineering, 1911, p. 601.

[2] Pring and Fairlie, Report of Eighth International Congress; Ipatiew, Jour. prakt. Chem., 1913, pp. 479–487; Pring and Fairlie, Jour. Chem. Soc., 1906, p. 1591; Ibid., 1911, p. 1796; Ibid., 1912, pp. 91–103; Bone and Coward, J. Chem. Soc., 1908, p. 1975. Proc. Chem. Soc., 1910, p. 146.

[1] Haber and co-workers, Jour. Gasb., 1896, pp. 377, 395, 435, 452; Hempel, Dissertation, Jour. Gasb., 1910, pp. 53, 77, 101, 137, 155.

the temperature goes above 800° C. the yield of hydrocarbons rapidly decreases; on the other hand, the hydrogen and carbon rapidly increase.
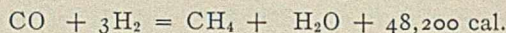
CARBURETED WATER GAS PROCESS

In the carbureted water gas practice as carried out to-day, there is a combination of the blue water gas and the oil gas process. Much is known about the blue gas; it is also known that this blue gas is carbureted by spraying in and cracking oil which furnishes the hydrocarbons and illuminants. There is little scientific information, however, regarding the interactions and equilibria which are reached when the two processes are combined. The formation of hydrocarbons and water from CO and H_2 or from CO_2 and H_2 is not theoretical speculation;[1] likewise the destruction of hydrocarbons with water to form CO and H_2 or CO_2 and H_2, as carried out in the all oil gas process, is not theoretical speculation. Whichever course prevails depends entirely upon conditions. Consequently, one is justified in concluding that the present composition of carbureted water gas is not the result of additive processes. Instead there is a mixture of blue water gas and cracked oil gas passing through the

carbureter and superheater which constitute a single unbalanced system of gases; naturally, there is a tendency to establish equilibrium between the constituents just as surely as there is a tendency to establish an equilibrium between the constituents of either the blue gas or the all oil gas when made individually. This equilibrium at the usual temperature of the superheater has fortunately favored the formation, or at least the preservation, of hydrocarbons. This fact, however, does not prove that the process is working under conditions of, or approaching, maximum efficiency. Nor does it prove that the present method of carbureting water gas is the most economical from the side of the quantity of gas oil consumed.

Many questions arise at this point. It might be possible to alter conditions in such a way as to solve or assist in solving the naphthalene and carbon problems of the gas manufacturer. It might still further be worth while to question the soundness of the natural

tendency of the American manufacturer to combine processes; it may appear that the attempt to do everything in a single vat rather than carry it out in stages is not the most economical method in the end.

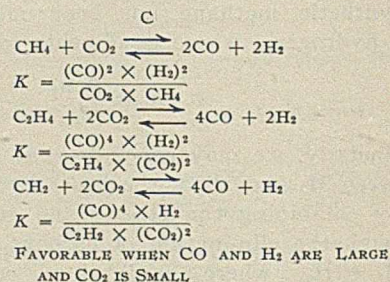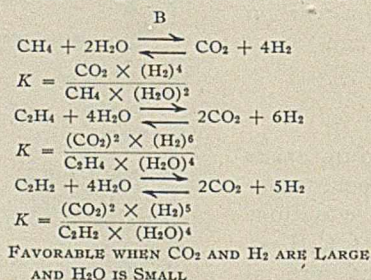### EQUATIONS AND THEORETICAL EQUILIBRIA INVOLVED

The formation of methane from carbon monoxide and hydrogen, or from carbon dioxide and hydrogen is an exothermic reaction and consequently is favored by low temperatures, although at these low temperatures a greater amount of time is required for complete reaction. The reaction may be greatly stimulated by catalytic agents such as nickel and cobalt. In view of the fact that there is a decrease in volume, one should expect pressure to be favorable to hydrocarbon formation. Equilibrium exists between CO and H_2 or CO_2 and H_2 on the one side and CH_4 and H_2O on the other.

$$CO + 3H_2 = CH_4 + H_2O + 48,200 \text{ cal.}$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O + 37,900 \text{ cal.}$$

with equilibrium established when

$$K = \frac{p_{CO}\, p^3_{H_2}}{p_{CH_4} p_{H_2O}} \text{ and } K' = \frac{p_{CO_2}\, p^4_{H_2}}{p_{CH_4} p^2_{H_2O}}$$

TABLE I—QUALITATIVE STUDY OF EQUILIBRIA

A	B	C
$CH_4 + H_2O \rightleftarrows CO + 3H_2$	$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$	$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$
$K = \dfrac{CO \times (H_2)^3}{CH_4 \times H_2O}$	$K = \dfrac{CO_2 \times (H_2)^4}{CH_4 \times (H_2O)^2}$	$K = \dfrac{(CO)^2 \times (H_2)^2}{CO_2 \times CH_4}$
$C_2H_4 + 2H_2O \rightleftarrows 2CO + 4H_2$	$C_2H_4 + 4H_2O \rightleftarrows 2CO_2 + 6H_2$	$C_2H_4 + 2CO_2 \rightleftarrows 4CO + 2H_2$
$K = \dfrac{(CO)^2 \times (H_2)_4}{C_2H_4 \times (H_2O)^2}$	$K = \dfrac{(CO_2)^2 \times (H_2)^6}{C_2H_4 \times (H_2O)^4}$	$K = \dfrac{(CO)^4 \times (H_2)^2}{C_2H_4 \times (CO_2)^2}$
$C_2H_2 + 2H_2O \rightleftarrows 2CO + 3H_2$	$C_2H_2 + 4H_2O \rightleftarrows 2CO_2 + 5H_2$	$CH_2 + 2CO_2 \rightleftarrows 4CO + H_2$
$K = \dfrac{(CO)^2 \times (H_2)^3}{C_2H_2 \times (H_2O)^2}$	$K = \dfrac{(CO_2)^2 \times (H_2)^5}{C_2H_2 \times (H_2O)^4}$	$K = \dfrac{(CO)^4 \times H_2}{C_2H_2 \times (CO_2)^2}$
FAVORABLE WHEN CO AND H_2 ARE LARGE AND H_2O IS SMALL	FAVORABLE WHEN CO_2 AND H_2 ARE LARGE AND H_2O IS SMALL	FAVORABLE WHEN CO AND H_2 ARE LARGE AND CO_2 IS SMALL

Combining the two equations with elimination of H_2O,

$$2CO + 2H_2 = CH_4 + CO_2 + 58,500 \text{ cal.}$$
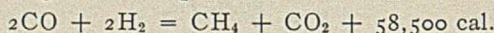
$$K'' = \frac{p^2_{CO} p^2_{H_2}}{p_{CH_4} p_{CO_2}}$$

In like manner the equilibria between CO, CO_2, and H_2O, on the one side, and C_2H_4, C_2H_2 and H_2O on the other, are considered below:

$$C_2H_4 + 2H_2O = 2CO + 4H_2 - 44,000 \text{ cal.}$$
$$C_2H_4 + 4H_2O = 2CO_2 + 6H_2 - 23,400 \text{ cal.}$$
$$C_2H_2 + 2H_2O = 2CO + 3H_2 - 500 \text{ cal.}$$
$$C_2H_2 + 4H_2O = 2CO_2 + 5H_2 - 20,100 \text{ cal.}$$
$$C_2H_4 + 2CO_2 = 4CO + 2H_2 - 64,600 \text{ cal.}$$
$$C_2H_2 + 2CO_2 = 4CO + H_2 - 21,100 \text{ cal.}$$
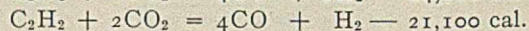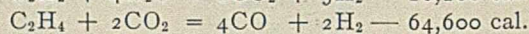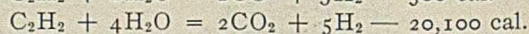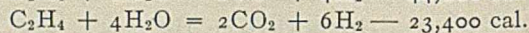
With these there is sufficient data to determine in a *qualitative* way the concentration conditions favorable to the methane, ethylene and acetylene desired in the resultant gas (see Table I).

The original complex state of affairs is thus partially clarified. One sees that conditions favorable to the formation of hydrocarbons, or at least unfavorable to the decomposition of hydrocarbons, exist when in

A, B and C there is an excess of H_2,

A and C, there is an excess of CO,

A and B, there is a minimum of water vapor,

B, there is an excess of CO_2,

C, there is a minimum of CO_2.

[1] Mayer, Henseling and Altmayer, *J. f. Gasb.*, **1909**, pp. 166, 194, 238, 326; P. Sabatier, *Chem. Ztg.*, **1913**, p. 148; P. Sabatier, Fr. Patent 355,325, **1905**; *Ibid.*, 355,900, **1905**; *Ibid.*, 361,616; *Ibid.*, 400,656; Eng. Patent 14,971, **1908**; *Ibid.*, 27,045; L. Vignon, Fr. Patent 416,699, **1909**; *Compt. rend.*, **1913**, pp. 131–134; Gautier, *Ibid.*, **1910**, p. 1565; Elsworthy and Williamson, Eng. Patent 12,461, **1902**; Bedford and Williams, Eng. Patents 17,017, 22,219, **1909**; H. J. Coleman, *Jour. Gas Lighting*, **1908**, p. 683; E. Erdmann, *Jour. f. Gasb.*, **1911**, pp. 737–743; E. Orlow, *Jour. Russ. Phys. Chem.*, **1908**, p. 1588; P. Jockum, *Jour. f. Gasb.*, **1914**, pp. 73, 103, 124, 149; T. Holgate, *Gas World*, **1914**, p. 90; German Patents 183,412, 190,201, 191,026, 237,499, 226,942, 177,703, 174,343 and 250,909.

An excess of hydrogen is favorable under any conditions; a minimum of water vapor is favorable under any conditions; an excess of CO appears to be favorable under any conditions; in the case of CO_2, however, one condition indicates an excess as favorable whereas another indicates an excess as unfavorable.

INFLUENCE OF TEMPERATURE ON EQUILIBRIUM CONDITIONS

While these qualitative relations are extremely valuable in the consideration of favorable conditions, they do not give a sufficiently concrete idea of the conditions which prevail at different temperatures. Each equilibrium constant has a definite value for a definite temperature. If this value of K is considered for 500° C. the reaction may proceed in one direction; whereas on considering the value of K' for the same reacting agents at 900° C., the reaction may proceed in the opposite direction. Qualitative expressions point merely in general directions and give no ideas as to maxima or minima in the curve of favorable conditions. As a matter of fact, taking the equilibrium

$$K = \frac{p_{CO} \; p^3_{H_2}}{p_{CH_4} \; p_{H_2O}}$$

where K equals approximately 0.001 for 500° C.; at 900° C. the equilibrium constant for the same relationship has the approximate value K' 346 or 346,000 times as great. This illustrates the importance of getting numerical figures for the constants expressing equilibrium conditions for the various gases, even though they be approximate.

Taking the CO, H_2, CH_4, and H_2O equilibrium under consideration, it appears that excesses of H_2 and CO would be favorable to the formation or preservation of hydrocarbons both at 500° C. and 900° C. It will further appear, however, that at 900° C. the excess of H_2 and CO to stimulate the reaction towards hydrocarbons will have to be enormous, while at 500° C. it need be only moderate. This can be seen from a mathematical observation of the equilibrium purely aside from the chemistry involved. At 500° C. the denominator is obviously the predominant factor. At 900° C. the numerator has become the predominant factor. In fact the situation is so different that it would take many times as much H_2 and CO at 900° C. as it would at 500° C. Taking the two equilibrium constants and calculating theoretical mixtures the following contrasting results are obtained:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

X = final volume CO   ½ (1 — 4X) = final volume CH_4
3X = final volume H_2 ½ (1 — 4X) = final volume H_2O

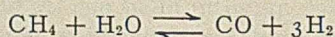$$K = \frac{p_{CO} \; p^2_{H_2}}{p_{CH_4} \; p_{H_2O}} = \frac{108 \; X^4}{16 \; X^2 - 8 \; X + 1}$$

Temp. °C.	$K_{calc.}$	Percentages			
		CO	H_2	CH_4	H_2O
500	0.001	5	15	40	40
900	346	24.3	72.9	1.4	1.4

The water vapor of these equilibria is usually not considered in practice because it never appears in either the gas of the tank holder or in the gas sampling tube and resulting analysis. This does not prove its absence in the machine. Also equal pressures of hydrogen and CO in a given system are not necessarily of the same influence. This is shown in equilibrium conditions for the CH_4, H_2O, CO and H_2 system, where for instance H_2 is raised to the third power, while the CO is of the first power. In view of the fact that in manufacturing practice the total pressure is approximately one atmosphere, the partial pressures are expressed by such decimals as 0.5. The third power of 0.5, or 0.125, is much less than the first power, 0.5. In other words, that constituent whose partial pressure is raised to the smaller power is of greater positive influence in determining the direction of the reaction, so long as the partial pressures are expressed by decimals.

Examples to show the effect of temperature on the state of equilibrium can be found in straight hydrocarbon reactions. The equilibrium between acetylene and benzene shows the following results:

	600° C	900° C	2000° C
$K = \dfrac{C_6H_6}{(C_2H_2)^3}$	9×10^{23}	1.2×10^{13}	6×10^{-4}

It appears that the value of K' at 2000° C. is 1.5×10^{27} times as great as the value of K at 600° C. This leads to the expectation that while at 600° C. the tendency is for all the acetylene to polymerize to benzene, at 2000° C., under proper conditions of pressure, the tendency is for the benzene to depolymerize to acetylene.

In the equilibrium existing between ethane and ethylene, $C_2H_6 = C_2H_4 + H_2 - 37900$ cal.

the value of K' at 900° is approximately 1.28, whereas the value of K at 150° is approximately 0.00000000000007. Ethane at 900° C. has a pronounced tendency to go to ethylene; the tendency for the ethylene to combine with hydrogen at 150° to form ethane is even more pronounced. The relatively small amount of ethane in oil gas made at 900° C. would seem to verify the first equilibrium constant; the large yield of ethane through the reduction of ethylene with hydrogen in the presence of palladium at 150° C. indicates the second constant.

EFFECT OF PRESSURE ON GASEOUS REACTIONS

In passing from ethane to acetylene, $C_2H_6 = C_2H_2 + 2H_2$, there is an increase in the number of volumes; on the other hand, when acetylene polymerizes to benzene, $3C_2H_2 \longrightarrow C_6H_6$, there is a decrease in the number of volumes. According to the principle of LeChatelier one would not expect the same pressure conditions to be favorable to both. Again, the information is qualitative and gives no concrete idea of the relative influence of one-third atmosphere when added to one atmosphere pressure absolute as compared to adding the same one-third atmosphere to ten atmospheres pressure absolute. As a type reaction consider

$$A \longrightarrow 2B \text{ where } K = \frac{B^2}{A}$$
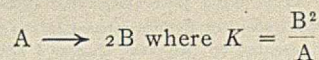
For numerical illustration, assume the value of K to be equal to 1 (any other value serving equally well). From this, one finds for partial pressures,

when A = 100, B = 10 or when A = 0.01, B = 0.1. In the first case the partial pressure of A is ten times as great as that of B; in the second case the partial

$$A \rightarrow 2B, \quad \frac{B^2}{A} = K = .1, \quad \therefore B = \sqrt{.1A}$$

CURVE I—REACTION ISOTHERM

pressure of A is only one-tenth as large as the partial pressure of B. In other words, by simply changing the total pressure on the system and keeping all other conditions constant, the ratio of A to B for the pressures shown has been divided by 100. By taking the first differential of the relationship, and equating it to 0,

$$K = \frac{B^2}{A} \qquad A = \frac{B^2}{K}$$

$$\frac{dA}{dB} = \frac{2B}{K} = 0 \qquad \therefore B = 0$$

one sees there is a maximum or minimum in the ratio of A to B as zero pressure is approached. By taking the second differential

$$\frac{d^2A}{dB^2} = +\frac{2}{K}$$

one finds the sign to be positive, indicating that the partial pressure of A as compared with the partial pressure of B approaches a minimum as the pressure approaches the absolute zero; or conversely there would be a maximum relative yield of B the closer one approached zero pressure absolute. The rate of change can best be seen by determining points for the parabola, $B^2 = KA$, and plotting the resulting curve.[1]

[1] Since most of the values of K encountered in the practical study of the problem were represented by decimals, Curves I and II were plotted on the basis of $K = 0.1$.

The general relationship of B to A changes only in degree the greater the change in the number of volumes, as can be seen by considering the curve for

$$A \rightarrow 3B \qquad K = \frac{B^3}{A} \qquad B^3 = KA$$

From the curves shown, one can readily see that the effect of reducing pressure from one atmosphere to two-thirds of an atmosphere gives an advantage which is of little practical consequence when compared with the advantage gained by the same reductions when nearer the absolute zero of pressure. One-thirtieth of an atmosphere added to one-thirtieth atmosphere pressure doubles the total pressure on a system just as effectually as an increase from 100 to 200 atmospheres.

EFFECT OF CONCENTRATION IN GASEOUS REACTIONS

The addition of an end product in any decomposition or dissociation process, such as

$$PCl_5 \longrightarrow PCl_3 + Cl$$
$$NH_4Cl \longrightarrow NH_3 + HCl$$
$$2SO_3 \longrightarrow 2SO_2 + O_2$$
$$2NH_3 \longrightarrow N_2 + 3H_2$$

checks the decomposition or dissociation. In other words, less PCl_5 will dissociate in an atmosphere of chlorine than in an atmosphere of nitrogen or air. Ammonium chloride when heated in an atmosphere of

$$A \rightarrow 3B, \quad \frac{B^3}{A} = K = .1, \quad \therefore B = \sqrt[3]{.1A}$$

CURVE II—REACTION ISOTHERM

ammonia will not dissociate to the same extent as in a vacuum or in an atmosphere containing neither ammonia nor hydrochloric acid gas. Likewise it would be expected that ethylene would not decompose to the same degree when subjected to a high temperature in

the presence of hydrogen as when subjected to the same temperature in an atmosphere of nitrogen. Further, if the ethylene were subjected to the same high temperature in the presence of both hydrogen and methane, these two constituents in the ethylene–methane–hydrogen equilibrium could be in excess; as a result, less of the ethylene should be decomposed in the formation of methane and hydrogen. Broadly speaking, to crack petroleum in an atmosphere containing all the hydrocarbon gases with the exception of ethylene, one would expect all the fixed gas coming from the petroleum to be ethylene, at least until the ethylene content of the system is sufficient to conform to the equilibrium conditions. The consideration of these principles seems to question the necessity of using valuable gas oil in continually generating new end products, such as tar and hydrogen; if they could be artificially supplied the equilibrium conditions would be satisfied without producing new decomposition and polymerization end products.

COMBINED INFLUENCE OF PRESSURE AND CONCENTRATION ON GASEOUS REACTIONS

Theoretical consideration of the effect of pressure on gaseous reactions indicates that an increased yield of gaseous hydrocarbons will be obtained as the total pressure on the system approaches zero; also an increased yield of illuminants will be obtained by cracking the oil in an atmosphere of end products such as hydrogen and methane. On combination the logical conclusion is that one should obtain the maximum yield of illuminants by cracking the petroleum at low pressures and in an atmosphere of end products. Upon first consideration one might reasonably question the idea of adding hydrogen or methane to a vacuum, but this investigation deals with relative partial pressures, regardless of whether the total pressure equals fifty atmospheres or one-fiftieth of one atmosphere absolute.

INFLUENCE OF CATALYSTS ON GASEOUS REACTIONS

Catalytic agents such as platinum, palladium, cobalt and nickel do not, in any way, influence final conditions of equilibrium; they merely hasten the rate at which the system reaches its final equilibrium. Whereas ethylene and hydrogen do not combine to an appreciable degree when heated to 100° C. in the absence of a catalyzer, the same mixture passed over colloidal palladium heated to 100° C. unites to form a considerable percentage of ethane. Likewise CO and H_2 or CO_2 and H_2 can be in intimate contact at 200° to 300° without appreciable reaction in the formation of methane, but when the same proportions are brought together in the presence of a catalytic agent such as nickel or cobalt there is a very large yield of methane and water.[1] Vignon[2] finds that lime has much the same effect on the combination of CO and H_2.

THE VAN'T HOFF DIFFERENTIAL EQUATION SHOWING THE RELATION OF K TO K'

To all students of physical chemistry the proposi-

tion of Berthelot and Thomson that "every chemical change gives rise to the production of those substances which occasion the greatest development of heat" is familiar. Were this true, it would be easy to predict which of two given reactions would take place at a given temperature. Chemists today recognize the fallacy of the statement because in all chemical reactions one deals with the additional so-called "latent energy." Berthelot's principle disregards this molecular energy, and assumes the free energy, termed maximum work, to be equal to the total energy change. Nernst maintains that this is true only at the absolute zero, *i. e.*, the entropy of liquids and solids at absolute zero temperature equals zero.

The van't Hoff equation showing the relation between K and K' is expressed by

$$\frac{d}{dT}(\log e\ K_p) = \frac{-q_p}{RT^2} \text{ or } d(\log e\ K_p) = \frac{-q_p}{R}\frac{dT}{T^2}$$

Upon integration this becomes

$$\log e\ K_p = \frac{q_p}{RT} + \text{constant}$$

Were it a simple matter to determine the value of this constant of integration, as well as the value of q at the different temperatures (in other words integrate the expression to absolute units) this would constitute a mathematical expression for what some consider a third law of thermodynamics. As yet there is no such accepted integration, and the best solution is to use approximate expressions, remembering at all times that the expressions are approximate, and making intelligent use of them as such. It is possible to avoid the constant of integration, however, by integrating between limits p' and p to

$$\log e\ K_{p'} - \log e\ K_p = \frac{q_p}{R}\left(\frac{1}{T^1} - \frac{1}{T}\right)$$

This integrated expression is extremely important in determining the value of K' for any desired temperature after the value of K for any other temperature has been experimentally determined. It is also of value in showing relationships between K and K' for two different temperatures, where neither has been determined, but in this case it expresses relationships and not direct values. For instance, assume that one wished to find the relationship between K and K' for the reaction

$$2C + H_2 = C_2H_2 - 58100 \text{ cal.}$$
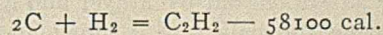
at the temperatures 600° and 900° C.

$$\log e\ K_{p'} - \log e\ K_p = \frac{-58100}{2}\left(\frac{1}{1173} - \frac{1}{873}\right) = 8.49$$

$$\log e\ \frac{K_{p'}}{K_p} = 8.49 \text{ or, } \log_{10}\frac{K_{p'}}{K_p} = 3.69$$

whence

$$K_{600} = \frac{K_{900}}{4900}$$

THE NERNST APPROXIMATION FORMULA FOR K

Even though correct, K is a value based on the assumption that sufficient time elapses to allow the system to reach complete equilibrium. When dealing

[1] Mayer, Henseling and Altmayer, *Jour. f. Gasb.*, **1909**, pp. 166, 194; Jockum, *Ibid.*, **1914**, pp. 73, 103, 124, 149; Orlow, *Jour. Russ. Phys. Chem.*, **1908**, p. 1588.
[2] Vignon, L., *Compt. rend.*, **1913**, pp. 131–134.

with hydrocarbons at different temperatures, this must not be overlooked. In fact the time element is of such primary moment that numerically correct values for K would be of little more practical use in gas manufacture than approximate values. In the case of reacting gases one does not have the speed conditions that ordinarily exist in solutions. On the other hand, gases brought together at sufficiently high temperatures do reach equilibrium practically instantly. It is important to bring out these limitations despite the value of approximate quantitative expressions such as the Nernst formula; they are of immense value in predicting the tendency of a reaction. In this paper the expression is merely used; its derivation with comments can be found in the seventh German edition of Nernst's "Theoretical Chemistry," Jellinek's "Physikalische Chemie der Gasreaktionen," or Sackur's "Thermochemie und Thermodynamik."

$$\log K = \frac{q}{4.571 T} + \Sigma v \, 1.75 \log T + \Sigma v C$$

where q is the heat developed at ordinary temperatures and under constant pressure, as taken from thermochemical tables; Σv represents the volume changes, and $\Sigma v C$ represents a summation of constants. These constants are given as follows:

H_2	1.6	C_2H_6	2.6	C_2H_2	3.2	CO	3.5	H_2O	3.6
CH_4	2.5	C_2H_4	2.8	C_6H_6	3.0	CO_2	3.2	O_2	2.8

To use Nernst's words, the equation gives a "fairly accurate" idea of the state of equilibrium in a system. The approximation is applied in this fashion:

$$C + 2H_2 = CH_4 + 18900 \text{ cal.}$$

$$\log K_{600} = \frac{+18900}{4.571 \times 873} - 1.75 \log 873 - 0.7 = -1.11 = \overline{2}.89 (a)$$

$$\log K_{750} = \frac{+18900}{4.571 \times 1023} - 1.75 \log 1023 - 0.7 = -1.93 = \overline{2}.07$$

$$\log K_{900} = \frac{+18900}{4.571 \times 1173} - 1.75 \log 1173 - 0.7 = -2.55 = \overline{3}.45$$

whence,

$$K_{600} = 0.077 \qquad K_{750} = 0.012 \qquad K_{900} = 0.003$$

(a) Negative logarithms must be converted into logarithms with positive mantissa.

In similar manner, the values of K, K', and K'' for Equations 1, 2, 3, 4, 5, 6, 7, 13, 16, 17, 18, and 22 in Table II have been calculated. In those reactions involving CO and CO_2, as 19, 23, and 26, use has been made of the approximation formulas for the same as worked out by Mayer and co-workers,[1] but substituting the values of q shown in the table.

CALCULATION OF HEATS OF REACTIONS FOR DIFFERENT EQUILIBRIA

The heat absorbed or emitted in a given reaction was determined by means of the ordinary thermochemical methods of addition and subtraction, as in the following typical examples:

(a) $2C + 8H = 2CH_4 + 37800 \text{ cal.}$
$2C + 4H = C_2H_4 - 14600 \text{ cal.}$
$2CH_4 = C_2H_4 + 2H_2 - 52400 \text{ cal.}$

(b) $6C + 6H = 3C_2H_2 - 174300 \text{ cal.}$
$6C + 6H = C_6H_6 - 11300 \text{ cal.}$
$3C_2H_2 = C_6H_6 + 163000 \text{ cal.}$

[1] Mayer, Henseling and Altmayer, *Jour. Gasb.*, **1909**, pp. 166, 194, 238.

(c) $C + 2H_2 = CH_4 + 18900 \text{ cal.}$
$2H + O = H_2O + 58300 \text{ cal.}$
$CH_4 + H_2O = 3H_2 + C + O - 77200 \text{ cal.}$
$C + O = CO + 29000 \text{ cal.}$
——————————
$CH_4 + H_2O = 3H_2 + CO - 48200 \text{ cal.}$
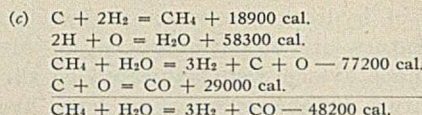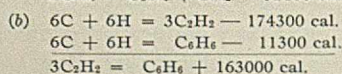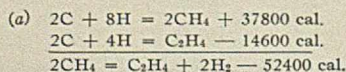
It is likewise possible to combine the values of K for one reaction with K' for a second reaction in order to determine K'' for the resultant reaction.

$$C + 2H_2 = CH_4 \qquad K = \frac{p_{CH_4}}{p^2_{H_2}}$$

$$2C + H_2 = C_2H_2 \qquad K' = \frac{p_{C_2H_2}}{p_{H_2}}$$
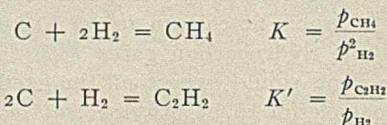
Dividing the square of the methane equilibrium by the acetylene equilibrium, one gets

$$K'' = \frac{(K')}{(K)^2} = \frac{p_{C_2H_2} p^4_{H_2}}{p_{H_2} p^2_{CH_4}} = \frac{p_{C_2H_2} p^3_{H_2}}{p^2_{CH_4}}$$

This operation can be represented by the equation

$$2CH_4 = C_2H_2 + 3H_2$$
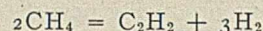
In this work the values of K and K' have been combined in the manner just shown in order to determine values for equations 8, 9, 10, 11, 12, and 14. The Nernst approximation formula could be applied directly to each of these equations with the same results. All reactions indicated in Table II may go in either direction. Attention is again called to the fact that the reactions given must be used with a consideration of all factors involved; no equation by itself represents a complete system. All the gases mentioned, together with many others, are tending to reach equilibrium with one another. Tar compounds were not listed. Benzene, C_6H_6, has been used as typical of all tar formations. In technical practice one gets benzene and other tar compounds from methane hydrocarbons; from experimental evidence, it is known that from ethylene[1] or acetylene[2] the same results are reached. Throughout the literature one finds questions as to whether methane goes to acetylene, or acetylene to methane, ethane to ethylene, ethylene to ethane, etc. Considered in the light of this study it appears that regardless of which hydrocarbon is used initially there is a pronounced tendency for the system to reach a common equilibrium dependent upon the existing temperature. With hydrocarbons the result seems to depend more upon conditions of temperature, pressure and concentration than upon the initial hydrocarbons. In other words, with proper conditions of temperature, pressure and concentration, and with sufficient time for complete reaction, the final equilibrium will be that of the mentioned hydrocarbons and their reaction products, regardless of whether decane, hexane, ethane, methane, ethylene or acetylene,[3] singly or in mixtures, are used in the beginning.

Table II furnishes the basis for the experimental work of this research. Its interpretation serves as a guide in determining the direction of experiments.

[1] Ipatiew, *Ber.*, **1911**, p. 2978; Ipatiew and Rontala, *Ibid.*, **1913**, p. 1748.
[2] R. Meyer, *Ibid.*, **1912**, p. 1609; Meyer and Tanzen, *Ibid.*, **1913**, p. 3183.
[3] W. A. Bone, *Jour. f. Gasb.*, **1908**, p. 803; D. T. Day, *Am. Chem. Jour.*, **1886**, p. 153; V. Lewes, *Proc. Roy. Soc.*, **1894**, p. 90; Worstall and Burwell, *Am. Chem. Jour.*, **1897**, p. 815; Bone and Coward, *Jour. Chem. Soc.*, **1908**, p. 1197; Sabatier and Senderens, *Compt. rend.*, **130**, 1559; C. Paal, *Chem. Ztg.*, **1912**, p. 60; Ipatiew, *Ber.*, **44**, 2987.

Taking Equation 9 as typical, where $K_{600} = 0.0000001$ and $K_{900} = 0.0004$, it seems advisable to exceed 900° C. in temperature. However, referring to $K_{600} = 0.077$ and $K_{900} = 0.003$ for Equation 3, it is evident that the rate at which methane would decompose to carbon and hydrogen, in accordance with Equation 3, might easily be sufficient to offset all C_2H_4 formation, in accordance with Equation 9.

Considering Equations 16 and 19, two of the most vital in present carbureted water gas manufacture, one finds

		K_{600}	K_{750}	K_{900}
16	$C + H_2O \rightleftharpoons CO + H_2$......	0.2	3.1	25.0
19	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$..	0.06	8.7	346.0

and that a temperature of 900° C. is favorable to the CO and H_2 formation of 16, but unfavorable to the methane preservation in Equation 19. On the other hand, a temperature of 600° C. is unfavorable to preservation of CO and H_2 in Equation 16 but is more favorable than 900° to hydrocarbon formation or preservation. Also it is more favorable to formation of CO_2 as shown by Equation 17. These temperature effects can be

TABLE II—QUANTITATIVE STUDY OF EQUILIBRIA

No.	REACTIONS	HEATS OF REACTION.	VOLUME CHANGES	(Formulas refer to partial pressures)	APPROXIMATE		
					K_{600}	K_{750}	K_{900}
1.	$C + O_2 \rightleftharpoons CO_2$..............	+97650	1 to 1	$K = \dfrac{CO_2}{O_2}$	6.9×10^{24}	1.9×10^{21}	4×10^{18}
2.	$CO_2 + C \rightleftharpoons 2CO$............	—39650	1 to 2	$K = \dfrac{(CO)^2}{CO_2}$	0.1	3.9	59.0
3.	$C + 2H_2 \rightleftharpoons CH_4$.............	+18900	2 to 1	$K = \dfrac{CH_4}{(H_2)^2}$	0.077	0.012	0.003
4.	$2C + 3H_2 \rightleftharpoons C_2H_6$............	+23300	3 to 1	$K = \dfrac{C_2H_6}{(H_2)^3}$	2.2×10^{-7}	1.7×10^{-8}	2.5×10^{-9}
5.	$2C + 2H_2 \rightleftharpoons C_2H_4$............	—14600	2 to 1	$K = \dfrac{C_2H_4}{(H_2)^2}$	6.0×10^{-10}	1.6×10^{-9}	3.2×10^{-9}
6.	$2C + H_2 \rightleftharpoons C_2H_2$............	—58100	1 to 1	$K = \dfrac{C_2H_2}{H_2}$	1.1×10^{-13}	1.5×10^{-11}	5.7×10^{-10}
7.	$6C + 3H_2 \rightleftharpoons C_6H_6$............	—11300	3 to 1	$K = \dfrac{C_6H_6}{(H_2)^3}$	1.2×10^{-15}	1.7×10^{-15}	2.2×10^{-15}
8.	$C_2H_6 \rightleftharpoons C_2H_4 + H_2$........	—37900	1 to 2	$K = \dfrac{C_2H_4 \times H_2}{C_2H_6}$	0.0027	0.094	1.28
9.	$2CH_4 \rightleftharpoons C_2H_4 + 2H_2$........	—52400	2 to 3	$K = \dfrac{C_2H_4 \times (H_2)^2}{(CH_4)^2}$	0.0000001	0.00001	0.0004
10.	$2CH_4 \rightleftharpoons C_2H_2 + 3H_2$..........	—95900	2 to 4	$K = \dfrac{C_2H_2 \times (H_2)^3}{(CH_4)^2}$	1.86×10^{-11}	0.0000001	0.00006
11.	$C_2H_4 \rightleftharpoons C_2H_2 + H_2$..........	—43500	1 to 2	$K = \dfrac{C_2H_2 \times H_2}{C_2H_4}$	0.00018	0.0093	0.178
12.	$C_2H_6 \rightleftharpoons C_2H_2 + 2H_2$..........	—81400	1 to 3	$K = \dfrac{C_2H_2 \times (H_2)^2}{C_2H_6}$	0.0000005	0.00089	0.228
13.	$C_4H_8 \rightleftharpoons 2C_2H_4$..............	—31800	1 to 2	$K = \dfrac{(C_2H_4)^2}{C_4H_8}$	1.41	31.6	258.0
14.	$3C_2H_2 \rightleftharpoons C_6H_6$............	+163000	3 to 1	$K = \dfrac{C_6H_6}{(C_2H_2)^3}$	9×10^{23}	5×10^{17}	1.2×10^{13}
15.	$3C_2H_4 \rightleftharpoons C_6H_6 + 3H_2$..........	+32500	3 to 4	$K = \dfrac{C_6H_6 \times (H_2)^3}{(C_2H_4)^3}$	5.5×10^{12}	4.1×10^{11}	6.7×10^{10}
16.	$C + H_2O \rightleftharpoons CO + H_2$........	—29300	1 to 2	$K = \dfrac{CO \times H_2}{H_2O}$	0.2	3.1	25
17.	$C + 2H_2O \rightleftharpoons CO_2 + 2H_2$.......	—19000	2 to 3	$K = \dfrac{CO_2 \times (H_2)^2}{(H_2O)^2}$	0.4	2.5	11
18.	$H_2O + CO \rightleftharpoons CO_2 + H_2$.......	+10350	2 to 2	$K = \dfrac{CO_2 \times H_2}{H_2O \times CO}$	1.95	0.81	0.42
19.	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$......	—48200	2 to 4	$K = \dfrac{CO \times (H_2)^3}{CH_4 \times H_2O}$	0.06	8.7	346.0
20.	$C_2H_4 + 2H_2O \rightleftharpoons 2CO + 4H_2$...	—44000	3 to 6	$K = \dfrac{(CO)^2 \times (H_2)^4}{C_2H_4 \times (H_2O)^2}$	...	...	...
21.	$C_2H_2 + 2H_2O \rightleftharpoons 2CO + 3H_2$...	—500	3 to 5	$K = \dfrac{(CO)^2 \times (H_2)^3}{C_2H_2 \times (H_2O)^2}$	...	...	...
22.	$C_6H_6 + 6H_2O \rightleftharpoons 6CO + 9H_2$...	—164500	7 to 15	$K = \dfrac{(CO)^6 \times (H_2)^9}{C_6H_6 \times (H_2O)^6}$	1.2×10^{-7}	0.49	48000
23.	$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$....	—37900	3 to 5	$K = \dfrac{CO_2 \times (H_2)^4}{CH_4 \times (H_2O)^2}$	0.3	16	280
24.	$C_2H_4 + 4H_2O \rightleftharpoons 2CO_2 + 6H_2$...	+23400	5 to 8	$K = \dfrac{(CO_2)^2 \times (H_2)^6}{C_2H_4 \times (H_2O)^4}$	...	...	...
25.	$C_2H_2 + 4H_2O \rightleftharpoons 2CO_2 + 5H_2$...	+20100	5 to 7	$K = \dfrac{(CO_2)^2 \times (H_2)^5}{C_2H_2 \times (H_2O)^4}$	...	...	...
26.	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$....	—58500	2 to 4	$K = \dfrac{(CO)^2 \times (H_2)^2}{CH_4 \times CO_2}$	0.017	5	354
27.	$C_2H_4 + 2CO_2 \rightleftharpoons 4CO + 2H_2$....	—64600	3 to 6	$K = \dfrac{(CO)^4 \times (H_2)^2}{C_2H_4 \times (CO_2)^2}$	...	...	...
28.	$C_2H_2 + 2CO_2 \rightleftharpoons 4CO + H_2$......	—31100	3 to 5	$K = \dfrac{(CO)^4 \times H_2}{C_2H_2 \times (CO_2)^2}$	...	...	...

more clearly understood by reference to the first numerical problem cited, and to the theoretical mixtures given for Equation 19 at temperatures of 600° and 900° C. It appears impossible to find a temperature favorable to both when the two reactions are simultaneously carried out. In order to preserve the hydrocarbons it becomes necessary to form H_2O, CO_2 and deposit carbon; or in order to avoid forming water vapor, CO_2 and deposit carbon, it becomes necessary to destroy hydrocarbons. The two cannot be reconciled.

SUMMARY

On theoretical grounds, therefore, it appears:

I—Possible to so create conditions that the oil cracking process can be carried out at a higher temperature than is now used in oil gas processes, and thereby greatly increase the yield of valuable hydrocarbons.

II—Possible to "crack" oil without depositing carbon, and without the formation of water vapor and CO_2.

III—Possible to partially control the quantity and composition of "tar" produced in gas manufacture.

IV—Impossible to preserve hydrocarbons and at the same time avoid CO_2, water vapor, and deposited carbon, when oil is "cracked" as in the present carbureted water gas process.

Interpretation of Table II and the results which could be expected in gas reactions, involving the constituents shown, could be expanded indefinitely. That these theoretical considerations are of more than academic interest will be brought out in subsequent papers.

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A METHOD FOR THE DETERMINATION OF MAGNESIUM IN CALCIUM SALTS [1]

By J. C. HOSTETTER

In the course of the preparation of some calcium silicates for thermal study, certain samples of calcium carbonate were tested to determine their suitability as sources of lime. Analyses of these samples showed that, of the non-volatile impurities determined by the makers, the amounts reported by them were substantially correct for all elements [2] except magnesium. This element was found to be present to the extent of several tenths of a per cent as oxide, even though the salts analyzed were of the very highest grades obtainable, and the makers' analyses had shown but a "trace," or, at most, 0.005 per cent MgO. A discrepancy of this large order could hardly be passed over without investigation, even though the problem thus presented was but a mere side issue. The writer's results on these samples had been obtained by the calcium sulfate separation, but, since the laboratory manipulation of this method was too involved for routine testing when large samples were taken, a method was developed by means of which very small amounts

of magnesium could be determined in the presence of much calcium, and which involved only the simplest laboratory manipulation. After this method had been developed, a number of calcium salts, from both domestic and foreign makers, were tested to determine their suitability for the particular problem in hand, but the surprisingly large quantities of magnesium found to be present were the source of much disappointment. In a few cases, the makers' results were of the same order of magnitude as those obtained by the new method, but usually the magnesia actually present was from fifty to even several hundred times greater than that reported by the maker. The probable source of the observed differences will appear in what follows.

Most of the methods employed for the determination of magnesium in the presence of calcium involve a removal of the latter by precipitation and a subsequent estimation of the former in the filtrate. In general, when testing for minute amounts of impurity, the procedure of first removing the main element by precipitation should never be followed. In some cases it can be justified, but these are rare and they can be determined only by direct test; in the greater number of cases the precipitating salt carries with it a large portion, if not all, of the impurity, and hence the amount of the latter subsequently found is much less than that actually present. Many methods of separation which are excellent when applied to tests in which the elements to be separated are present in nearly equal amounts fail utterly when the one element is present to the extent of a thousand times that of the other. This latter condition is the main one involved in the problem here studied, and failure to recognize this is the general reason why chemical manufacturers have often failed to find all of the magnesium present in their calcium salts. The specific manner in which loss of magnesium may occur in the ordinary methods of separating calcium and magnesium will appear in the discussion which follows.

REMOVAL OF CALCIUM AS OXALATE—The extensive investigation of Richards, McClaffrey and Bisbee [1] on the occlusion of magnesium by calcium oxalate has shown that when the latter is precipitated in the presence of magnesium under certain conditions, the resulting calcium oxide may carry as much as 16.4 per cent MgO; under the usual conditions for this precipitation, the occlusion may still amount to about 1 per cent. Only with careful attention to the details of the method proposed by them can a satisfactory separation of calcium from magnesium be made with one precipitation of the calcium oxalate.

Ordinarily, in exact analysis, two precipitations of the oxalate are deemed necessary for a good separation, and when the elements are present in nearly the same amount, this is justified. When large amounts of calcium and mere traces of magnesium are present, however, two precipitations, or even more, will not separate these two elements quantitatively.

In view of the convincing character of the work

[2] With the possible exception of sodium, for which the makers' "trace" was found to be 0.02 per cent Na_2O.

[1] *Z. anorg. Chemie*, **28** (1901), 71; *Proc. Am. Acad. Arts Sci.*, **36** (1901), 375.

cited above, it is indeed surprising that texts on the subject of reagent testing should continue to prescribe the determination of magnesium in a solution from which calcium has been removed as oxalate, when calcium salts are to be tested for this impurity. As carried out by Krauch,[1] and by Krauch-Merck,[2] the calcium of 1 gram of the salt is precipitated as oxalate and the salt is considered satisfactory if sodium phosphate solution gives no precipitate in the filtrate on standing twelve hours.

REMOVAL OF CALCIUM AS SULFATE—This separation, as outlined by Classen,[3] is comparatively free from the errors inherent in the oxalate and carbonate precipitations. That calcium sulfate precipitated in the presence of magnesium carries a negligible amount of magnesia (occluded or otherwise) is shown by the following experiment: The calcium of 5 grams of a pure calcium chloride in alcoholic solution was precipitated with sulfuric acid in the presence of 250 mg. MgO (added as chloride). The calcium sulfate was filtered off and washed with 50 per cent alcohol in the prescribed manner. After drying, the magnesia was determined in this calcium sulfate by the new method to be described shortly, and found to be but 0.005 per cent.[4] In many cases the magnesia thus lost would be insignificant, but this loss could not be tolerated in the analysis of the purest calcium salts.

Though this method of removing calcium is fairly satisfactory in regard to the amount of magnesia occluded, it has the disadvantage that when large amounts of calcium are to be removed, the laboratory manipulation becomes difficult. This is due to the bulky nature of the precipitated calcium sulfate, the many tedious washings of the precipitate which are required, and the evaporation to dryness of several liters of alcoholic solution. Accordingly, we have discontinued the use of this method except as an occasional check.

The discrepancy observed between the makers' magnesia determinations and the writer's results by the calcium sulfate separation can be completely accounted for on the reasonable assumption that the makers follow the oxalate separation as given in the standard texts on reagent testing. Direct evidence on this point is generally lacking, but in the case of one maker at least, the labels specify that the salt has been tested according to Krauch.[5] In the absence of specific information on this subject from the other makers,[6] we can only assume that their results were also secured with the calcium oxalate separation on a comparatively small sample.

REMOVAL OF CALCIUM AS CARBONATE—It is well known that the separation of calcium as carbonate involves the same source of error as the oxalate separa-

tion—some magnesium is occluded by the calcium carbonate. The extent of this occlusion is indicated by the amount of MgO remaining in calcium carbonates of the highest grade—about 0.08 per cent.[1]

THE METHOD OF HILDEBRAND AND HARNED—This excellent method for the determination of magnesium in the presence of calcium (and other metals) is a precipitation of the magnesium as hydroxide, the precipitant being sodium hydroxide and the changes in hydrogen ion concentration being followed by means of the hydrogen electrode.[2] Since the uncertainty in the end point, as given by them, may amount to as much as 4 mg. MgO, it is evident that this method could be used in connection with the present problem only in the case of highly impure calcium salts.

THE PROPOSED METHOD

The essential feature of the method that follows is the *concentrating* of the magnesium from a large sample of the salt being tested into a precipitate containing but a small proportion of the calcium. After this has been accomplished the ordinary methods may be used to separate these elements with satisfactory results, since the ratio CaO : MgO is no longer 1,000 or 10,000 : 1, but has been reduced to 10 or 100 : 1. This concentrating is effected by precipitating the magnesium as hydroxide by adding either calcium oxide (made, in many cases, by ignition of the salt itself) or a solution of sodium hydroxide in slight excess over that necessary to precipitate the magnesium.[3] The details of the method follow.

Ten grams of the calcium salt are brought into solution in water, and the volume made up to 100 cc. If acid is used to bring the salt into solution, the excess is neutralized with sodium hydroxide, *after* the expulsion of CO_2, SO_2, etc., by boiling. The calcium oxide made from 0.3 to 0.5 gram[4] calcium carbonate by ignition is now added and the solution heated to boiling; the precipitate is filtered off but not washed. The precipitate is dissolved in dilute hydrochloric acid and the calcium removed by two precipitations with ammonium oxalate. The filtrates from these two precipitates are combined and the magnesium in this combined filtrate is determined by precipitation as ammonium magnesium phosphate with microcosmic salt. This precipitation is easily brought about by shaking in a stoppered flask. After standing several hours, the precipitate is filtered off, washed free from phosphoric acid with 10 per cent ammonia, and finally ignited to magnesium pyrophosphate which is weighed.

FACTORS AFFECTING THIS METHOD

I. SOLUBILITY OF CALCIUM HYDROXIDE IN SOLUTIONS OF CALCIUM CHLORIDE—A knowledge of the solubility of calcium hydroxide in 10 per cent calcium chloride solution is necessary in order to determine the amount

[1] "Testing of Chemical Reagents," 3 ed., p. 60.
[2] "Chemical Reagents, Their Purity and Tests," p. 80.
[3] "Ausgewählte Methoden d. Anal. Chem.," Erster Band, p. 835.
[4] In this connection, it is interesting to note that magnesium is occluded less by precipitating barium sulfate than any other metal which has been studied. Allen and Johnston, *J. Am. Chem. Soc.*, **32** (1910), 612; Johnston and Adams, *Ibid.*, **33** (1911), 832.
[5] Merck and Company, "Blue Label Reagents."
[6] Requests for information on this point were ignored by an American maker.

[1] The average of the MgO contents of the calcium carbonates given in Table II.
[2] *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **1**, 217; *J. Am. Chem. Soc.*, **35** (1913), 867.
[3] Compare the method of analysis of high-grade zinc by F. Mylius and O. Fromm, in which they concentrate the impurities into a sulfide precipitate containing very little zinc. *Z. anorg. Chem.*, **9** (1895), 149.
[4] This need be weighed only to 5 per cent. The amount to be used depends on the MgO content of the salt. Cf. *postea*.

of calcium oxide to be added to the chloride solution. The calcium oxide must be added in amount somewhat more than sufficient to saturate the solution with respect to calcium hydroxide, and to precipitate the magnesium as hydroxide. From the data of Zahorsky[1] and of Lunge,[1] we find that 100 cc. of a 10 per cent calcium chloride solution will dissolve 0.13–0.14 gram calcium oxide at 80° to 100°. One gram of calcium carbonate yields 0.560 gram calcium oxide, and for the precipitation of 1 gram magnesia there is required 1.392 grams calcium oxide. These figures, together with the solubility, show that the calcium oxide made from 0.5 gram calcium carbonate will saturate the solution and is in slight excess over that required to precipitate 0.100 gram MgO—equal to 1 per cent on a 10 gram sample. Similarly, calculation shows that 0.4 gram calcium carbonate will precipitate 0.6 per cent MgO in a 10 gram sample, and 0.3 gram calcium carbonate will precipitate 0.2 per cent MgO. It is obviously of great advantage to use the smallest possible amount of calcium oxide in this precipitation, and, for most salts, the oxide from 0.3 gram calcium carbonate suffices.

II. SOLUBILITY OF MAGNESIUM HYDROXIDE IN CALCIUM CHLORIDE SOLUTIONS SATURATED WITH CALCIUM HYDROXIDE—No information on this subject has been found in the literature. We have qualitatively estimated the effect of this solubility on the method, and have concluded that it is nearly negligible. The tests were made by determining the magnesia in 10 gram portions of a certain sample of calcium chloride, keeping all conditions constant except the volume of the solution in which the magnesium hydroxide was precipitated. This volume was varied from 25 cc. to 200 cc. The results showed that the change of solubility with increasing dilution is, fortunately, small. We have accordingly chosen the 10 per cent dilution as a convenient volume in which to work and one in which the error due to solubility is probably not over 0.2 mg. MgO for 100 cc.

This crude method of investigating the solubility of magnesium hydroxide in solutions of calcium chloride saturated with calcium hydroxide was made necessary on account of the difficulty of obtaining calcium salts free from magnesium and magnesium salts free from calcium. It was thought to be beyond the scope of this paper to prepare suitable materials and actually determine this solubility. One experiment on the solubility of magnesium hydroxide in calcium hydroxide solution saturated at 90° was made by determining the magnesium in the liquid phase after having removed the calcium as sulfate. The magnesia in 100 cc. of this solution is probably less than 0.1 mg., since the precipitate of ammonium magnesium phosphate was too small to be filtered off and weighed.

III. USE OF SODIUM HYDROXIDE AS THE PRECIPITANT—It is obvious that a known amount of sodium hydroxide may be used to precipitate the magnesium and a slight excess of calcium hydroxide. Where acid has been used to bring a calcium salt into solution,

[1] As given by Seidell, "Solubilities of Inorganic and Organic Substances," p. 91, 1st ed.

the excess acid is carefully neutralized, using methyl orange as indicator, and then an amount of sodium hydroxide solution is added, sufficient to precipitate the magnesium and a slight amount of calcium hydroxide. From this point on, the procedure is exactly as outlined under the calcium oxide precipitation.

In the work of Hildebrand and Harned quoted above, it is mentioned that the change in hydrogen ion concentration when the magnesium hydroxide has all been precipitated and the calcium hydroxide is beginning to precipitate, is too gradual to be shown by an indicator. Nevertheless, it was hoped that an indicator could be found by the change of which an indication would be given, when sodium hydroxide was used, that the hydrogen ion concentration corresponding to a precipitation of some small amount of calcium hydroxide had been reached. Several indicators of appropriate turning point (10^{-12} to 10^{-13}) were tested, but the results obtained were erratic. This was partly due to the fact that there are comparatively few indicators giving sharp color changes in this region of hydrogen ion concentration, and very probably also that there was a large "salt effect" due to the highly concentrated calcium chloride solution.

THE PRECISION OBTAINABLE by the hydroxide concentration method, and the agreement between it and the sulfate separation, are shown in Table I.

TABLE I—PERCENTAGES OF MAGNESIA

Sample	By hydroxide concentration	By sulfate separation
A	0.091	0.074
	0.091	0.090
	0.089	...
	0.090	...
B	0.25	0.25

These analyses on carefully mixed samples of calcium carbonate were run side by side. On still another sample of calcium carbonate, the writer obtained 0.09 per cent MgO, using the new method with but one precipitation of the oxalate, while Dr. H. S. Washington, of this laboratory, found 0.12 per cent MgO, using the same method but making two careful precipitations of the calcium oxalate. The difference is about what would be occluded by the first precipitate of calcium oxalate.

NOTES ON THE METHOD—Since the effect of the salts of other acids on the solubility of magnesium hydroxide in calcium chloride solutions saturated with calcium hydroxide has not been determined, it is advisable to ignite such calcium salts as the nitrate, acetate, formate, and oxalate to oxide, and then dissolve all but a portion equivalent to the 0.3–0.5 gram of $CaCO_3$, in dilute hydrochloric acid, using methyl orange as indicator. The reserved portion of oxide is added as the precipitant, thus removing the possibility of introducing magnesium as an impurity in the calcium oxide made from calcium carbonate, or in the sodium hydroxide. The carbonate, hydroxide, oxide, sulfite, and sulfate should be dissolved directly in hydrochloric acid.

Traces of calcium as tricalcium phosphate are frequently present to the extent of some 0.3–0.5 mg. in

the magnesium pyrophosphate, and may be corrected for by dissolving the ignited (and weighed) precipitate in a little dilute sulfuric acid, adding alcohol, and allowing to stand over night. The calcium sulfate is filtered off and weighed as such; or it may be converted into oxalate and weighed as oxide.

It is obvious that there is practically no limit to the size of the sample from which the magnesium can be concentrated by this method, thus allowing almost any desired precision in the amount of magnesium weighed. A 10 gram sample will permit of 0.001 per cent MgO being

on the magnesia content of *all* the samples tested by the new method. As will be seen by an inspection of the table, these samples are from all of the more widely known makers of analyzed chemicals. In presenting these results there is absolutely no discrimination, and we think that a comparison of the makers' determinations as given in the table will support our statement that all the makers are equally at fault in this particular. We publish these data not as a criticism of the makers, but solely to present the facts in the case as we find them, with the hope that their publication

TABLE II—MAGNESIA FOUND IN HIGH-GRADE CALCIUM SALTS FROM DIFFERENT MAKERS

SALT	MAKER	DESCRIPTION	LOT NO.	Maker's analysis	Hydroxide concentration method	MgO calc. as per cent of CaO
				MAGNESIUM OXIDE		
Acetate......	B & A	"C.P."		No anal.	0.027%	0.076%
Acetate......	E & A	"Tested Purity"	B 83	—0.001%	0.041	0.11
Acetate......	J T B	"C.P." Analyzed	51313	—0.001	0.001	0.002
Carbonate....	B & A	"C.P." Analyzed		"Trace"	0.090	0.16
Carbonate....	B & A	"C.P." Analyzed		No anal.	0.25	0.44
Carbonate....	B & A	"Special"		No anal.	—0.001	0.00
Carbonate....	J T B	"C.P." Analyzed	8212	0.001	0.039	0.068
Carbonate....	J T B	"C.P." Special		—0.001	0.048	0.085
Carbonate....	J T B	"C.P." Analyzed	101212	0.001	0.056	0.10
Carbouate....	J T B	"C.P." Analyzed	5513	0.005	0.027	0.048
Carbonate....	J T B	"C.P." Analyzed	101613	0.005	0.10	0.17
Carbonate....	E & A	"Tested Purity"	B 33	0.005	0.27	0.48
Carbonate....	Kb	"Zur Anal. m. Garantieschein"	4782	0.000	0.062	0.11
Carbonate....	M	"Blue Label Reagent"	10853	Free	—0.001	0.00
Carbonate....	M	"Blue Label Reagent"	12303	Free	0.000	0.000
Carbonate....		Iceland Spar			0.047	0.084
Chloride......	B & A	"C.P." Fused Granular		"Trace"	0.058	0.11
Chloride......	J T B	"C.P." Analyzed Cryst.	103012	0.001	0.009	0.023
Chloride......	J T B	"C.P." Analyzed Cryst. (Diff. Bottle)	103012	0.001	0.006	0.015
Chloride......	J T B	"C.P." Analyzed Anhyd.	10912	0.001	0.042	0.083
Chloride......	J T B	"C.P." Analyzed Anhyd.	11612	0.001	0.15	0.29
Chloride......	J T B	"C.P" Analyzed Anhyd. (12-mesh)	121812	0.005	1.44	2.85
Chloride......	J T B	"C.P." Analyzed Anhyd.	112112	0.01	0.23	0.45
Chloride......	J T B	"C.P." Analyzed Cryst.	122211	0.002	0.065	0.17
Chloride......	M	"Blue Label Reagent" Fused	10353	Not det.	0.023	0.045
Formate......	J T B	"C.P." Analyzed	61812	None	0.005	0.038
Hydroxide....	J T B	"Technically Pure"	32213	0.05	0.87	1.14
Hydroxide....	M	"Blue Label Reagent"	1472	Not det.	0.68	0.89
Nitrate......	J T B	"C.P." Analyzed Cryst.	101712	0.001	0.14	0.59
Nitrate......	E & A	"Tested Purity"	B 13	None	0.31	1.31
Oxalate......	Kb	White Label	L 2801	No anal.	0.041	0.084
Oxide........	J T B	From Marble	32413	0.51	1.18	1.18
Oxide........	Kb	"Zur Anal. m. Garantieschein"		Not det.	0.77	0.77
Sulfate......	M	"Blue Label Reagent"	11513	Free	0.007	0.021
Sulfite.......	E & A	"Tested Purity" Cryst.	B 83	0.05	0.36	1.00

ABBREVIATIONS

B & A: Baker & Adamson Chemical Company, Easton, Pa.
J T B: J. T. Baker Chemical Company, Phillipsburg, N. J.
E & A: Eimer & Amend, New York, N. Y.
Kb: C. A. F. Kahlbaum, Berlin.
M: Merck & Company, New York, N. Y.

No anal.: No analysis on label.
Not det.: Analysis on label but MgO not determined.
Free: Free from MgO as tested by Krauch's method.
—0.001: Less than 0.001% MgO.

approximately determined. We have used at times samples of 20 and even 100 grams with this method.

The oxalate separation has been used after the hydroxide concentration in order to combine in one precipitation the removal of calcium and also the slight amounts of iron and aluminum which may be present. While the sulfate separation is undoubtedly the better, it requires an evaporation and a separate precipitation for the other impurities.

RESULTS OBTAINED BY THE HYDROXIDE CONCENTRATION METHOD—In Table II are given the results

may help to bring about the more complete elimination of magnesia from calcium salts, and hence to help raise the standard of analyzed chemicals. We think that in presenting the matter in this way, it is fairest both to the maker and to the user. With this presentation of the subject, our direct interest must end, since, as stated at the beginning, the problem was but a mere side issue, and further testing of calcium salts on our part has been rendered unnecessary, as we have secured by purchase enough of the purest of the lots tested to last us several years.

For many purposes where the highest grade calcium salts are used, the presence of much magnesia may be regarded as a matter of indifference. The two elements are chemically very similar; the reactions of one may not interfere with those of the other. Whether the presence of magnesium in calcium salts is objectionable for certain purposes or not is, however, aside from the main issue. The point to be emphasized is that the makers' analyses should represent exactly the amounts of impurities present. Only in this manner can the makers' analyses be of any real service to the user of analyzed chemicals.

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PARAFFIN BODIES IN COAL TAR CREOSOTE AND THEIR BEARING ON SPECIFICATIONS[1]

By S. R. Church and John Morris Weiss

In specifications for coal tar creosote, there is usually a paragraph stating that the oil shall be a pure product of coal tar, and free from adulteration with any oil or products from any other tar. The purpose of this clause is usually to provide against admixture with petroleum products, such as water gas tar or oil tar derivatives. In the present paper, the writers wish to consider one requirement which is sometimes introduced with the object of enforcing this provision.

Coal tar is made up mainly of aromatic compounds, and the presence of bodies belonging to the saturated paraffin series has been regarded by some as direct and unmistakable evidence of contamination of coal tar creosote by distillates from other tars.

Dean and Bateman[2] proposed a sulfonation test for creosote oils, based on the principle that aromatic hydrocarbons dissolve in concentrated sulfuric acid to sulfonic acids, while bodies of the paraffin series remain unattacked. They applied this test to numerous creosote oils, and concluded that any oil yielding a sulfonation residue was contaminated with products of other source than coal tar.

A modification of this test, devised by J. M. Weiss, was proposed in an article by S. R. Church,[3] which did not in any way change the results of the test, but merely made it easier of operation, so far as the detection of traces was concerned. Later Bateman[4] made further modifications in the test, which made it a still more convenient laboratory operation. This modification was endorsed by Church[5] after trial, as more convenient and practical than the earlier proposals.

Chapin[6] proposed the substitution of a dimethyl sulfate test to be used to determine paraffin hydrocarbons in creosote oil, as well as in creosote oil dips.

[1] Presented before the American Association for the Advancement of Science, Engineering Section, Atlanta, December 31, 1913.
[2] Dean and Bateman, "The Analysis and Grading of Creosotes," Forest Service, Circular 112.
[3] Church, This Journal, 3 (1911), 227.
[4] Bateman, "Modification of the Sulphonation Test for Creosote," Forest Service, Circular 191.
[5] Church, This Journal, 5 (1913), 195.
[6] Chapin, "Dimethyl Sulfate Test for Creosote Oils and Creosote Dips," Bureau of Animal Industry, Circular 167.

Reeve and Lewis[1] have used this test, and have given a number of results obtained by it.

A brief description of the tests in question may be useful in this connection.

SULFONATION TEST

"Ten cubic centimeters of the fraction of creosote to be tested are measured into a Babcock milk bottle. To this is added 40 cc. of 37 N sulfuric acid, 10 cc. at a time. The bottle with its contents is shaken for two minutes after each addition of 10 cc. of acid. After all the acid has been added, the bottle is kept at a constant temperature of from 98° to 100° C. for 1 hour, during which time it is shaken vigorously every ten minutes. At the end of an hour, the bottle is removed, cooled and filled to the top of the graduation with ordinary sulfuric acid, and then whirled for 5 minutes in a Babcock separator. The unsulfonated residue is then read off from the graduations."

DIMETHYL SULFATE TEST

"Five cubic centimeters of the fraction are pipetted into a narrow 25 cc. burette, and shaken with 8 cc. of dimethyl sulfate after closing the burette with a smooth, close-fitting cork. Separation of the residual oil occurs in a short time in the form of a clear, almost colorless, supernatant liquid layer."

We shall first briefly discuss the relative merits and demerits of the sulfonation test and the dimethyl sulfate test, and then consider in what manner the results of such a test should be interpreted, particularly as regards creosote oil specifications.

We have made some experiments using the dimethyl sulfate test, as recommended by Chapin, and the modified sulfonation test with fuming sulfuric acid and the Babcock bottle, as proposed by Bateman. Average samples of coal tar oil and water gas tar oil were distilled, and fractions taken from 240° to 270° C., and from 270° to 300° C. These fractions were then subjected to the dimethyl sulfate test and the sulfonation test, with the following results:

	Sulfonation test residue Per cent	Dimethyl sulfate test residue
Coal tar distillate 240–270° C.	1.2	0
Coal tar distillate 270–300° C.	2.0	0
Water gas tar distillate 240–270° C.	4.0	0
Water gas tar distillate 270–300° C.	6.8	0

Further tests on other oils were also made, with the following results:

	Sulfonation test residue Per cent	Dimethyl sulfate test residue Per cent
Water gas tar distillate 240–270° C.	2.4	0.0
Water gas tar distillate 270–330° C.	1.2	0.0
Mixed tar distillate 240–270° C.	2.0	0.0
Mixed tar distillate 270–330° C.	3.0	0.0
Blast furnace tar distillate 240–270° C.	17.6	23.0
Blast furnace tar distillate 270–330° C.	23.2	38.0
Oil tar distillate 240–270° C.	14.4	22.0
Oil tar distillate 270–330° C.	18.8	28.0

It can be seen from these results that the dimethyl sulfate method showed no residue in many oils that

[1] Reeve and Lewis, This Journal, 5 (1913), 293.

gave measurable residues by the sulfonation method, and we feel that the former test is of no value so far as the detection of small amounts of saturated hydrocarbons in the presence of aromatic hydrocarbons is concerned. Undoubtedly, if there were considerable amounts of petroleum or blast furnace tar distillates present, where there might be a sulfonation residue of from 10 to 20 per cent, the dimethyl sulfate test would detect it, but where there is only a question of comparatively small admixtures of material, itself low in sulfonation residue, this test would not seem to be of any value.

We have experienced great difficulty in obtaining dimethyl sulfate; moreover, we find that it changes rapidly on standing, so that fresh supplies must frequently be had. Another objection to this reagent is the danger attendant upon handling it.

In a great deal of our laboratory work on oils distilled from various kinds of tar, the results have been clouded by uncertainty as to the authenticity of the sample. Some time ago, therefore, we procured samples of tars from typical coke ovens and gas plants

above. In the appended table are given the results of these tests of the various oils examined, representative tests of each type of installation being selected. Where there were any great variations between oils of the same origin, the tests of the two most widely divergent materials examined are given.

A consideration of the creosote oil specifications in active use indicates a tendency toward the use of the sulfonation test. The requirements of the test vary widely; in one case, the sulfonation residue is limited to 10 per cent, in others to 1 per cent, while still others specify that in the fraction 300° to 360° C. it shall not exceed 0.25 cc.

In a Forest Service circular, C. P. Winslow[1] gives the requirement for Class 1 and Class 2 coal tar creosotes (the only ones considered by him as pure coal tar creosotes) that there shall be no sulfonation residue. In "mixed coal tar creosotes," he allows, in Class 1, 10 per cent of the 305–320° C. fraction as a sulfonation residue, and in Class 2, 20 per cent of the fraction 305–320° C., expressing it in the form that "the volume of the sulfonation residue in cubic centimeters should

SULFONATION RESIDUES OF OILS FROM AUTHENTIC SAMPLES OF TAR

Oils Derived From	Up to 210°	210–225°	225–235°	235–245°	245–255°	255–265°	265–275°	275–285°	285–295°	295–305°	305–320°	320–330°
Semet-Solvay coke oven tar	0	0	0	0	0	0	0	0	0	0	0	0
Koppers coke oven tar	0	0	0	0	0	0	0	0	0	0	0	0
United Otto coke oven tar	0	0	0	0	0	0	0	0	0	0	0	0
Horizontal gas retort tar	0.2	0.2	0.4	0.6	0.8	0.8	0.8	0.8	0.8	0.4	0.4	0.4
Inclined gas retort tar	2.0	2.0	2.0	4.0	5.6	6.4	5.2	6.4	6.0	5.6	5.2	4.0
Vertical gas retort tar	5.8	3.6	3.6	4.6	5.6	5.6	6.2	4.8	6.0	4.0	4.4	2.2
Water gas tar, 1	0.4	0.4	0.4	0.4	0.4	0.8	0.8	0.8	0.8	0.8	0.4	0.4
Water gas tar, 2	3.2	5.2	6.0	6.4	7.2	9.2	10.4	10.0	14.2	13.6	13.6	12.4
Oil tar	9.2	22.8	26.4	26.4	26.0	33.2	31.6	35.6	42.4	36.0	32.0	32.0
Blast furnace tar	...	11.6	14.4	16.4	17.2	20.4	21.2	22.0	20.8	20.4	18.0	16.4
Lignite tar	7.0	7.0	9.8	11.6	13.4	14.8	17.0	20.4	20.4	19.6	19.0	12.0

under such conditions as to make accidental contamination or admixture practically impossible. These tars were distilled to pitch, and the distillate oils recovered. The oils were subjected to a number of tests, partially along the lines of Dean and Bateman's work (*loc. cit.*). It is not our intention to give the details of this work at present, except in so far as they affect the question of the sulfonation test.

Coal tars may be divided into two classes:

1—Coke oven tars, which may be further subdivided according to the type of oven in which the coal is carbonized.

2—Gas works tars, which may be divided similarly into horizontal, inclined and vertical gas works tars.

In this investigation, we had one or more samples from each of the different types of installation, both coke oven and gas works, and have, we believe, examined a sufficient number of samples to draw correct conclusions.

The examination of the oils, which is of interest in this connection, was a Hempel distillation (made in accordance with the Forest Service method for analysis of creosote oil), taking fractions at the following temperatures, Centigrade:

210	235–245	265–275	295–305
210–225	245–255	275–285	305–320
225–235	255–265	285–295	320–330

These fractions were then subjected to the sulfonation test, using Bateman's modified method, as described

not be greater than one-tenth or one-fifth, respectively, of the weight of the fraction in grams."

In the opinion of the writers, the requirement of no sulfonation residue is unfair as a basis of classification of pure coal tar creosotes, and a very high limit for mixed creosotes, such as 10 to 20 per cent, is useless, in view of the fact that a great majority of the water gas tar distillates have considerably less than this amount of sulfonation residue in any fraction, and this makes it unnecessary, *per se*, to have any coal tar creosote at all present. If a requirement for no sulfonation residue should be enforced, only straight coke oven tars could be used to produce such creosote oils, and in most cases this is certainly a commercial impossibility. If a limit of 1 per cent is set, the coke oven tar oils and some of the horizontal gas works tar oils would meet the requirement, but some of the latter would require the admixture of coke oven tar oils to bring the residue below this limit. A requirement that the sulfonation residue shall not exceed 2 per cent would not be unfair, and would not ordinarily bar any normal coal tar creosote oils. It would prevent the addition to coal tar creosotes of large proportions of blast furnace oils and petroleum products other than those from water gas tar. The admixture of water gas tar distillates with coal tar creosote oil would, of necessity, have to be taken care of in some other way than by the sulfonation test, as it is very plain that cer-

[1] Winslow, "Commercial Creosotes," Forest Service, *Circular* 206.

tain mixtures of coke oven tar oil and water gas tar oil would show a lesser residue than certain other oils obtained wholly from gas works coal tars.

In conclusion, the authors believe that the sulfonation test in itself has been shown to be of comparatively little value in detecting the admixture of oils of petroleum origin, particularly those derived from water gas tar, with creosote oil.

In a later paper, we hope to publish additional data from our analyses of authentic tars, indicating the value of certain other tests as means for determining the origin of oils used for creosoting.

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A VOLUMETRIC METHOD FOR THE DETERMINATION OF LEAD

By ALFRED ALDER AND M. F. COOLBAUGH
Received February 16, 1914

The principles of the determination are based upon the precipitation and separation of the lead as sulfate, the solution of this precipitate in sodium hydroxide and the precipitation of the lead from the solution, after slightly acidifying it with nitric acid, by a solution of potassium iodate. The precipitate of lead iodate is dissolved in dilute hydrochloric acid. It is then titrated in the presence of a few cubic centimeters of chloroform, with a standard solution of ammonium sulfocyanate to the first appearance of a violet color in the chloroform.

The outline scheme for the analysis of an ore is as follows: Treat 0.5 to 1 gram with nitric acid, and, if necessary, with a small quantity of hydrochloric acid. Then add a few cc. of sulfuric acid and evaporate to dense fumes of sulfuric anhydride, leaving not more than 2 to 3 per cent of free sulfuric acid present when the solution is diluted to 100 cc. Cool the thoroughly decomposed material and add about 100 cc. of water, bring to a vigorous boil and add 10 to 15 cc. of alcohol. Cool and allow to stand until the precipitate has completely settled, and then decant upon a filter paper and wash the residue with a mixture of 1 per cent sulfuric acid and 10 per cent alcohol, and finally with the alcohol alone. Dissolve the lead sulfate in a small quantity of hot sodium hydroxide (10 to 15 cc. of a 10 per cent solution will usually be sufficient). Wash the residue and filter paper thoroughly with hot water, followed by hot water slightly acidified with nitric acid and finally by water slightly alkaline with sodium hydroxide. Add a few drops of phenolphthalein to the solution and a quantity of potassium iodate solution sufficient to precipitate all of the lead and have a small amount in excess. Heat the solution, and while hot add nitric acid (1.2 sp. gr.), drop by drop, until the pink of the phenolphthalein is discharged, and then 15 to 29 drops in excess. Bring the whole to a boil, cool slightly, add 15 to 20 cc. of alcohol and then cool to room or tap water temperature. Decant the solution through a filter paper and wash by decantation with one part of alcohol to three parts of water until the wash solution gives no test for iodate when treated with hydrochloric acid, chloroform and ammonium

sulfocyanate. Transfer the filter paper and precipitate to a 250 cc. stoppered flask. Wash out the precipitation vessel with 40 to 50 cc. of a cold solution of hydrochloric acid (1 vol. conc. HCl to 2.5 vols. water) and transfer to the flask with the main portion of the precipitate. Add 3 to 5 cc. of chloroform to the above solution and titrate at once with the standard ammonium sulfocyanate to the first violet which remains in the chloroform after vigorous shaking. For ores high in lead it is advisable to add to the flask before the end point is reached 10 to 15 cc. of cold HCl (1.1 sp. gr.).

NOTES ON THE DETERMINATION

The above method was tested out with purified lead sulfate and gave the following results:

G. PbSO₄ taken	G. Pb in PbSO₄	G. Pb found	G. PbSO₄ taken	G. Pb in PbSO₄	G. Pb found
0.3	0.2049	0.2047	0.3	0.2049	0.2046
0.3	0.2049	0.2038	0.3	0.2049	0.2044
0.3	0.2049	0.2056	0.3	0.2049	0.2045
0.3	0.2049	0.2052	0.4	0.2732	0.2728
0.3	0.2049	0.2049	0.2	0.1366	0.1369
0.3	0.2049	0.2051	0.1	0.0683	0.0684
0.3	0.2049	0.2049			

A number of ores were run by this method using 0.5 gram samples for the determinations. The lead in these ores had been previously determined by a careful analysis, weighing up the lead as the sulfate. The following are some of the results obtained:

No. ore	Lead by PbSO₄ method Per cent	Lead by iodate method Per cent
1	3.18	3.26
2	4.20	4.18
3	4.42	4.37
4	50.51	50.6
5	64.39	64.27

Ammonium acetate, sodium acetate and potassium hydroxide, as well as the sodium hydroxide were used in the solution of the lead sulfate obtained from the decomposition of the ore, or that which was used as the standard. From the ammonium acetate or sodium acetate solutions, either neutral or acid with acetic acid, the lead iodate precipitated slowly and incompletely. Boiling, long standing and a decided excess of potassium iodate tended to make the precipitation complete, but under most careful conditions gave quite decidedly low results. The potassium hydroxide gave equally as good results as the sodium hydroxide. It is difficult to wash the filter paper free from the solution obtained by the treatment of the lead sulfate with the sodium hydroxide. Experiments gave results as much as 10 per cent low. This difficulty is corrected by washing with dilute nitric acid followed by washing with a dilute solution of sodium hydroxide.

The solubility of lead iodate is given as 0.012 gram in a liter of water at 2° C. and 0.019 gram in a liter of water at 18° C. (Kohlrausch and Böttger). It is stated that its solubility in nitric acid is only slight, some authorities going so far as to say that it is insoluble in hot dilute nitric acid. Experiments were made to test this point. The precipitates of lead iodate were washed with hot dilute nitric acid and the lead content determined. The same was repeated using

the cold dilute acid. The following are a few of the results obtained:

Lead taken: 0.2049 gram
Lead found: 0.1969, 0.1995, 0.1957 and 0.1971 gram

When water was used to wash the precipitate, low results which would not agree with each other were obtained. In washing with nitric acid or water, the wash water could not be freed from iodate as given by the test with hydrochloric acid, chloroform and ammonium sulfocyanate. The solubility of the lead iodate in dilute HNO_3 with a slight excess of potassium iodate and alcohol present was shown by evaporating the filtrates from seven solutions out of which the lead had been precipitated as iodate according to the outline scheme. The original solutions contained 1.7 grams of lead. The solutions which were evaporated were fumed with H_2SO_4 and the lead determined as sulfate according to the regular method. The amount of lead sulfate found was 0.6 mg.

If lead iodate is precipitated in the cold it comes down in a flocculent form and is not readily purified. Unless an extra amount of time is taken in the washing the results will be high, due to the retention by the precipitate of some of the excess of potassium iodate. When the lead is precipitated hot, or boiled after precipitation it comes down with a coarsely crystalline structure. The precipitate settles rapidly and is readily purified from the excess iodate. Forty to fifty cc. of the alcoholic solution have proved ample for washing, even when 0.25 gram of lead in the form of iodate was being treated. Too much alcohol added to the solution at the precipitation of the lead iodate, or too strong an alcoholic solution used for washing purposes will make the removal of the excess of potassium iodate difficult, since this substance is much less soluble in alcohol than in water. Too much potassium iodate should not be added in excess because of the expense of the reagent, and the added difficulty of washing it out. It is important that the solution from which the lead is precipitated as iodate should be made distinctly acid with HNO_3, otherwise some lead will be present as the hydroxide and the results will be low. Lead iodate is decidedly soluble in an excess of a fixed alkali hydroxide.

The lead iodate is soluble in dilute cold hydrochloric acid without the decomposition of the iodate radical. If the hydrochloric acid is concentrated or the dilute solution hot, chlorine will be liberated and the iodate radical decomposed. This reaction can possibly be represented by the following equation:

$$12HCl + Pb(IO_3)_2 = 8Cl + 2ICl + PbCl_2 + 6H_2O$$
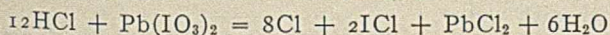
Whenever chlorine is liberated, the determination is ruined since the results will be decidedly low. The strength of hydrochloric acid used in the outline scheme will not liberate chlorine unless the solution is hot. The reaction between the lead iodate and the NH_4CNS is most rapid when the iodate is completely in solution. If, after the titration has been started, it is noticed that some of the iodate is not in solution, it is best to add more of the hydrochloric acid. The reaction of titration is:

$$3Pb(IO_3)_2 + 4NH_4CNS + 12HCl = 6ICl + 3PbCl_2 + 4NH_4Cl + 4H_2SO_4 + 4HCN + 2H_2O$$
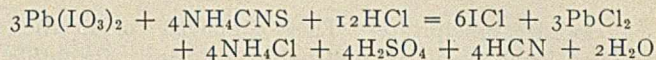
The end point is caused by the liberation of the I from the ICl and its absorption in the chloroform. The equation for the end point is probably the following:

$$6ICl + NH_4CNS + 4H_2O = 6I + NH_4Cl + H_2SO_4 + 5HCl + HCN$$
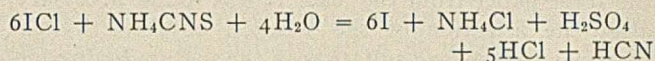
When sufficient hydrochloric acid is present the reaction of titration is a very rapid one, and the end point very sharp and distinct, leaving nothing to be desired in that direction. The approach to the end point is indicated by the rapidity of the discharge of a yellowish red color throughout the solution. The end point can, in fact, be determined quite closely even without the use of chloroform, by the permanent formation of this yellowish red color. The chloroform can be used over again by decanting off the larger portion of the filter paper pulp and solution and then adding the precipitate from another determination.

The ammonium sulfocyanate is made by dissolving about 2.5 grams of the pure salt in a liter of water and then standardizing it according to the well known Volhard method for silver by titrating a known silver nitrate solution which has been made by dissolving pure silver in nitric acid and boiling off the nitrous fumes. The silver standard of the ammonium sulfocyanate multiplied by 1.4398 gives the lead standard. The NH_4CNS may also be standardized by titration against c. p. lead sulfate or metallic lead. The above strength of solution will equal about 1 per cent of lead for each cubic centimeter when 0.5 gram sample is taken for analysis.

The elements encountered in the ordinary ore analysis which might interfere with the determination of the lead by giving insoluble iodates are barium, calcium, copper, silver, bismuth, mercury and ferric iron. Of these only the barium, calcium, silver and bismuth are likely to interfere since the copper and mercury can be completely removed and the ferric iron nearly removed from the lead by filtering them off from the insoluble lead sulfate formed in the decomposition of the ore. The solutions must contain calcium in rather large concentration before this element will precipitate as iodate under the conditions given for the lead determination. In no experiment tried was it found to interfere with the accuracy of the method for lead. Barium forms an insoluble iodate which is slightly soluble in dilute nitric acid, but barium sulfate is not affected by sodium hydroxide and only very slightly by dilute nitric acid, so that not enough of it is carried into solution to be precipitated as the iodate. Experiments with these two elements show their influences upon the determination.

G. $PbSO_4$ taken	G. $BaSO_4$ taken	G. $CaSO_4$ taken	G. Pb in $PbSO_4$	G. Pb found
0.3	0.1	...	0.2049	0.2052
0.3	0.2	...	0.2049	0.2046
0.3	0.2	0.1	0.2049	0.2042

It is difficult by the ordinary methods of treatment to remove all the silver and bismuth from the insoluble

lead sulfate precipitate. These elements form, when treated with sodium hydroxide solution, insoluble silver oxide and bismuth hydroxide which are readily soluble in dilute nitric acid. To keep these from going in with the lead solution, and at the same time to purify the filter paper from the lead, it was found necessary, after the filtration of the solution obtained by the treatment of the lead sulfate with the sodium hydroxide, to remove the filtrate and treat the residue and filter paper with hot water slightly acidified with nitric acid. The filtrate obtained by this treatment is made quite strongly alkaline with sodium hydroxide and filtered through the same filter paper. From the combined filtrates the lead iodate is precipitated. The following experiments show that these elements, when the treatment is made according to the above modifications of the outline scheme, have no effect upon the accuracy of the results. Ferric iron is not readily precipitated as the iodate in presence of nitric acid also has no effect upon the results.

G. PbSO₄ taken	G. Ag₂SO₄ taken	G. Fe₂(SO₄)₃ taken	G. Bi₂(SO₄)₃ taken	G. Pb in PbSO₄	G. Pb found
0.3	0.1	...	0.1	0.2049	0.2047
0.3	0.1	...	0.1	0.2049	0.2043
0.3	...	0.015	...	0.2049	0.2051

The determination of lead in an ore by this method can be made in 45 minutes to one hour's time. The cost of the reagents in the determination is not excessive, and should not exceed a few cents per determination when 0.5 to 1 gram samples are used. For low-grade lead ores the cost is materially reduced because of the smaller quantity of potassium iodate required. Some of the advantages of the determinations are rapidity of manipulation, definiteness of the reactions of titration, non-interference of the elements usually associated with lead minerals and exactness of the end point.

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THE DETERMINATION OF ARSENIC IN HYDROCHLORIC AND SULFURIC ACIDS

By R. F. TARBELL
Received January 22, 1914

It is always necessary in the manufacture and purchase of hydrochloric and sulfuric acids that are to be used in the preparation of food products to make some sort of test to determine the percentage of arsenic present.

The writer has worked out a method which he has found very satisfactory and accurate. Once the apparatus is set up and the standard solutions and reagents prepared, a determination requires very little attention.

PRINCIPLES INVOLVED

It is well known that arsine and iodine react together under certain conditions forming arsenious iodide. This reaction seems to hold when the iodine is dissolved in specially prepared gasoline. In the following method arsine is generated in the usual way, passed through a solution of lead acetate to remove any hydrogen sulfide formed and then passed through a known volume of an iodine-in-gasoline solution of known strength. The excess of iodine is reduced by adding a known amount of a sodium arsenite solution and then titrated back with an iodine solution using starch as indicator. The writer has found that by this method one atom of arsenic is equivalent to eight atoms of iodine. This would correspond to the following equations:

$$AsH_3 + 3I_2 = AsI_3 + 3HI$$
$$2AsI_3 + 3H_2O = As_2O_3 + 6HI$$
$$As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI$$
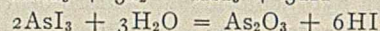
APPARATUS

A train is connected as follows: A 500 cc. flask is fitted with a two-hole rubber stopper. Through one hole in the stopper is fitted a 125 cc. globe-shaped separatory funnel turned up at its lower end to prevent the escape of gas. Through the other hole is fitted a Kjeldahl connecting bulb. This is in turn connected with a Koeninck's potash bulb. The potash bulb is next connected to a single bulb such as always comes with and precedes a Meyer's bulb tube. To this is connected a Meyer's bulb tube. There should be at hand a 500 cc. Squibb's pear-shaped separatory funnel.

REAGENTS AND STANDARD SOLUTIONS

Gasoline—A quantity of gasoline is prepared from ordinary 60° gasoline in the following way: Fill a gallon bottle three-fourths full of the gasoline and add 200 cc. C. P. sulfuric acid. Stir this eight or ten hours with air, let settle, pour off the gasoline into a similar bottle, add 200 cc. C. P. sulfuric acid as before and let stand several days with occasional shaking. Pour the gasoline from the acid, add a dilute solution of sodium hydroxide and agitate ten or fifteen minutes to neutralize all acid. Wash gasoline with water, let settle, and when clear it is ready for use.

Stannous Chloride Solution—Dissolve 25 grams C. P. tin in arsenic-free hydrochloric acid and evaporate almost to dryness. Take up with water and make up to 500 cc.

Arsenic-free Hydrochloric Acid—Dilute C. P. hydrochloric acid to sp. gr. 1.10, add a small amount of either copper sulfate or mercuric chloride and precipitate with hydrogen sulfide. Let stand four or five days, filter and distil.

Alkaline Sodium Arsenite Solution—Dissolve 0.2640 gram pure arsenious oxide and 1 gram sodium carbonate in 100 cc. hot water. After cooling, add 1 gram sodium bicarbonate and make total volume 1 liter with water.

Iodine Solution—Dissolve 0.6773 gram pure iodine and 1.2 grams potassium iodide in water and make the volume up to 1 liter.

Iodine-in-Gasoline Solution—Dissolve 0.6773 gram pure iodine in the prepared gasoline and make the volume up to 1 liter with gasoline.

Zinc—Use C. P. arsenic-free stick zinc.

METHOD OF ANALYSIS

Fill the potash bulb with lead acetate solution to the top of the first bulb. Put 20 cc. iodine-in-gasoline

solution, 80 cc. gasoline and 20 cc. water into the bulb tubes. Place a stick of zinc weighing about 35 grams in the flask and connect the apparatus, seeing that all joints are tight. Weigh out about 25 grams of the acid to be tested. The weight of sample and the quantity of iodine-in-gasoline solution used will of course vary with the arsenic content of the acid, but a little experience will enable the operator to adjust these quantities. If hydrochloric acid, its specific gravity should be made about 1.10 by adding either water or arsenic-free hydrochloric acid as may be necessary. If sulfuric acid, its specific gravity should be made about 1.40 by adding either water or c. p. sulfuric acid as may be necessary. Pour the sample through the separatory funnel into the flask. Then pour 1 cc. stannous chloride solution through the funnel. Pour through enough water to wash the funnel. Close the stopcock and let the reactions proceed with all connections tight for about 2 hours, heating the flask on a water bath if the action becomes too slow. Then add 20 cc. c. p. sulfuric acid (sp. gr. 1.40) through the separatory funnel and allow the test to proceed for 1 hour more. Empty the contents of the bulb tube into the 500 cc. separatory funnel. Wash the bulb tube with water into the same funnel. Run out the water from below and add 20 cc. sodium arsenite solution to the contents of the funnel. Shake till the solution is colorless, allow to settle into two layers and draw off the lower layer into a white dish. Add starch indicator and titrate with the iodine solution in the regular way: 1 cc. iodine solution = 1 cc. sodium arsenite solution = 1 cc. iodine-in-gasoline solution = 0.00005 gram arsenic.

RESULTS OBTAINED

Mg. As taken	Mg. I taken by As	Mg. As found	Mg. As taken	Mg. I taken by As	Mg. As found
0.02	0.34	0.02	0.50	6.73	0.50
0.02	0.27	0.02	0.50	6.42	0.47
0.05	0.61	0.04	1.00	13.45	0.99
0.05	0.74	0.05	1.00	12.90	0.95
0.10	1.15	0.08	1.88	25.12	1.85
0.10	1.42	0.10	2.50	34.07	2.51
0.25	2.98	0.22	3.75	50.58	3.73
0.37	4.86	0.36	....	.....	....

A number of analyses were made using different volumes of solutions of sodium arsenite of known strength. Kahlbaum's arsenious oxide was used in making these solutions. The numbers in the last column are obtained by multiplying the figures in the second column by 0.07382.

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ONE CAUSE OF LOW RESULTS IN THE ASSAY OF PEPPERMINT OIL

By HARRY W. REDFIELD
Received April 26, 1913

Articles in *Hygienic Laboratory Bulletin*, No. **49**, "Digest of Comments on the Pharmacopoeia of the United States of America" (Eighth Decennial Revision), pages 222 and 223, and in *Hygienic Laboratory Bulletin* No. **75**, "Digest of Comments on the Pharmacopoeia of the United States of America" (Eighth Decennial Revision), pages 395 to 396, point out the fact that low results are often obtained in the assay of peppermint oil.

One possible source of error that seems to have received no attention is the low efficiency of the reflux condenser that is employed when the oil is boiled for one hour with a $N/2$ alcoholic solution of potassium hydroxide, in the determination of menthol as ester; and later in the method when the oil is boiled for one hour with acetic acid anhydride, and also when the acetylized oil is boiled for one hour with a $N/2$ alcoholic solution of potassium hydroxide, in the determination of total menthol. Any oil lost through incomplete condensation would, obviously, cause low results.

Therefore, a number of determinations of menthol as ester and of total menthol were made on six different samples of peppermint oil obtained from as many sources. The three forms of condenser illustrated were used.

In Fig. 1 is shown the Allihn condenser.

-Fig.1-   -Fig.2-   -Fig.3-
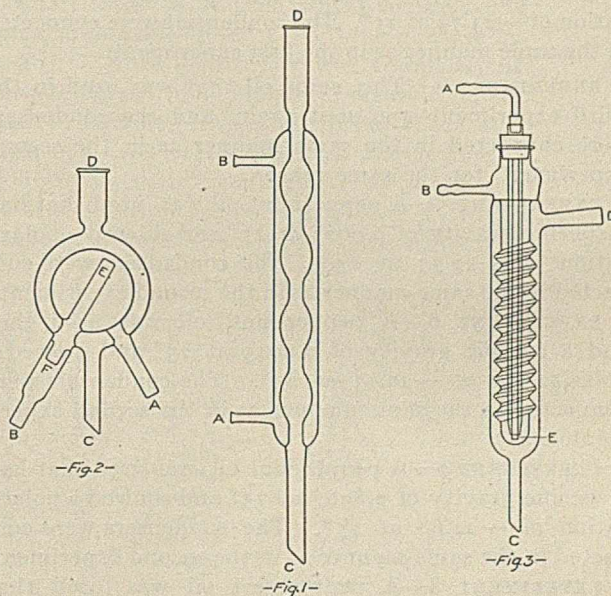
In Fig. 2 is shown the Chamot-Soxhlet glass ball condenser. The device at F is worthy of mention as it enables the experimenter to see at a glance how much water is flowing through the condenser.

In Fig. 3 is shown the Fritz Friedrichs condenser, which may be used as a reflux condenser by allowing the vapor to enter at C, or which may be used in distillations by allowing the vapor to enter at D. The water for cooling enters through AE and escapes through B.

EXPERIMENT 1—A peppermint oil was used that had a specific gravity of 0.9056 at 25° and showed a polarization of —19.87 at 25°. Equal volumes of the oil were weighed in three 125 cc. flasks and the required amounts of $N/2$ alcoholic potassium hydroxide added. Into the neck of one of the flasks was inserted an Allihn condenser, into the neck of another was inserted a Chamot-Soxhlet condenser, and into the neck of the third was inserted a Fritz Friedrichs condenser. The outlet D of each condenser was loosely plugged with cotton wool. The condensers were connected in series,

the cooling water first flowing through the Fritz Friedrichs condenser, then through the Chamot-Soxhlet condenser and finally through the Allihn condenser. Heat was supplied under the flasks by small ring burners and the assay followed out according to the Pharmacopoeia method.

EXPERIMENT 2 was made on the same oil that was used in EXPERIMENT 1; the direction of the cooling water was reversed and it was made to flow first through the Allihn condenser and finally through the Fritz Friedrichs condenser. The purpose of this was to ascertain whether any advantage had been given to the Fritz Friedrichs condenser in the previous experiment, by reason of the fact that the temperature of the water flowing through the condensers was found to be 2.1° higher when it entered the Allihn condenser than it was when it entered the Fritz Friedrichs condenser, in the first experiment.

EXPERIMENT 3—A peppermint oil was used that had a specific gravity of 0.9002 at 25° and showed a polarization of —24.73 at 25°. The condensers were connected in the same manner as in the first experiment.

EXPERIMENT 4—The same oil that was used in the third experiment was used again, and the condensers were connected in the same manner as in the second experiment, for the same reason.

EXPERIMENT 5—A peppermint oil was used that had a specific gravity of 0.9021 at 25° and showed a polarization of —20.37 at 25°. The condensers were connected in the same manner as in the second experiment.

EXPERIMENT 6—A peppermint oil was used that had a specific gravity of 0.9045 at 25° and showed a polarization of —20.03 at 25°. The condensers were connected in the same manner as in the second experiment.

EXPERIMENT 7—A peppermint oil was used that had a specific gravity of 0.8987 at 25° and showed a polarization of —24.88 at 25°. The condensers were connected in the same manner as in the second experiment.

EXPERIMENT 8—A peppermint oil was used that had a specific gravity of 0.9010 at 25° and showed a polarization of —26.34 at 25°. The condensers were connected in the same manner as in the second experiment.

The analytical results obtained in these eight experiments are given in the following table:

Exp. No.	Friedrichs Condenser % menthol		Soxhlet Condenser % menthol		Allihn Condenser % menthol	
	As ester	Total	As ester	Total	As ester	Total
1	7.97	64.98	7.98	64.49	7.76	58.06
2	7.94	64.39	7.89	64.34	7.74	58.10
3	6.61	70.30	6.71	70.09	6.26	65.58
4	6.59	69.23	6.57	69.20	6.23	64.97
5	9.33	63.74	9.28	63.59	9.02	60.20
6	8.23	60.19	8.17	60.07	7.84	55.72
7	8.97	69.42	9.07	69.26	8.59	64.57
8	8.43	58.36	8.40	58.40	8.03	54.07
Average	8.01	65.08	8.01	64.93	7.68	60.21
Variation from max	0.00	0.00	0.00	—0.15	—0.33	—4.87

SUMMARY

While the results obtained when using either the Fritz Friedrichs condenser or the Chamot-Soxhlet condenser were almost the same, the results were 0.33 per cent low for menthol as ester and 4.87 per cent low for total menthol when the Allihn condenser was used.

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OBSERVATIONS UPON THE ASSAY OF DIGESTIVE FERMENTS[1]

By Howard T. Graber

In a previous paper, "Some Observations upon the Assay of Digestive Ferments," appearing in THIS JOURNAL I gave a résumé of tests applied in standardizing Digestive Ferments, with special reference to their peculiarities. A second paper, "Influence of Size and Shape of Bottles upon the Assay of Pepsin," appearing in the *Journal of the American Pharmaceutical Association* (Vol. II, No. 12, December, 1913), deals with the assay of pepsin. Further observations with these sensitive *enzymes* have shown the following peculiarities with:

PANCREATIN

In the first mentioned paper I called attention to the fact that in assaying diastasic ferments for starch hydrolyzing power, the kind of starch used is very important, and that the use of potato starch gives an activity $1/3$ greater than that given when corn starch is used. I now want to carry this statement further and show that one can use two different samples of the same kind of starch; for instance, two samples of corn starch, and unless the physical properties of the two samples are identical, the results will be of wide variation. Of these physical properties *reaction* is the most important. The U. S. P. says the starch should be *neutral* to litmus paper, but as a matter of fact, litmus paper is not sufficiently sensitive. I have found that if the corn starch is slightly acid to cochineal indicator, this acidity slightly accelerates the activity of the enzyme, although litmus paper would show the starch to be neutral, and further, a strength of acid in the starch which would show acid to litmus paper, would inhibit the activity of the diastase.

On the other hand, a slight alkalinity in the starch, shown by cochineal solution, would inhibit the diastasic activity, although here again the alkalinity would be so slight as to cause the starch to appear neutral to litmus paper. The following experiment will illustrate these points:

Starch No.	Moisture Per cent	Ash Per cent	Reaction to litmus	Reaction to cochineal	Acid equivalent in HCl abs. by wt.	Equivalent in Per cent KOH	Activity of same sample of pancreatin shown
1	6.66	0.1	Neutral	Slightly acid	0.0023	...	1 : 25 in 4 mins.
2	4.66	0.18	Neutral	Alkaline	....	0.031	1 : 25 in 10 mins.
3	6.66	0.1	Neutral	Neutral	....	...	1 : 25 in 4 mins. 15 secs.

The table shows that starch No. 1, in which the pancreatin tests 1:25 in 4 mins., has an acidity by cochineal of 0.0023 per cent HCl absolute by weight, although it

seems neutral to litmus paper, and if this acidity be carefully neutralized, the diastase requires 15 seconds more to hydrolyze the starch and if now the starch be made to have an alkalinity equivalent to 0.031 per cent KOH, the activity of the pancreatin changes from 1 : 25 in 4 mins. to 1 : 25 in 7 1/2 mins., although the starch still meets the U. S. P. requirements and is neutral to litmus paper.

It would therefore appear to one unaccustomed to working with these enzymes that the pancreatin had lost some of its diastasic activity, when the real truth of the matter is that the presence of the slight alkalinity in the starch inhibited the starch hydrolyzing power of the diastase.

The percentage moisture in the corn starch on the market varies, but a difference of 2 per cent more or less is not an important factor, as the following figures show.

If the diastase tests 1 : 25 in 5 minutes on starch of 4.66 per cent moisture, it tests 1 : 25.5 in 5 minutes on starch of 6.66 per cent moisture, or 1 : 25 in 4 minutes 54 seconds: i. e., 2 per cent more moisture in the starch, or what is the same thing, 2 per cent less starch, showed the disatase to have an acceleration of but 6 seconds. However, a difference in moisture content as great as 10 per cent would show a decided effect upon the final strength of the diastase, but the average samples of starch would not vary to such an extent.

It is my custom, before adopting a sample of starch for diastasic assay, to wash it thoroughly with 10 times its volume of distilled water and after drying to determine its moisture and ash content, then to shake it up with neutral, recently boiled and cooled, distilled water, and after filtering to test the filtrate with cochineal indicator, and to make use of the starch only when it shows neutral to this indicator. As a further check, I test a known sample of pancreatin with it.

A third precaution to eliminate variations in assay, is to use always a diluted iodine solution of the same temperature. A warm iodine solution does not show the starch iodide reaction so readily as a cold one.

These three precautions then should always be observed if uniform results are to be obtained:

I—The starch should be neutral or at most but very weakly acid.

II—It should be chosen of average moisture content with a preference toward the use of anhydrous starch.

III—The temperature of the diluted iodine solution should be constant.

DIGESTIVE FERMENTS COMPANY
DETROIT

LABORATORY STUDIES ON MALT EXTRACT[1]

By Howard T. Graber

Some years ago I started an investigation upon the concentrated glycerine extracts of malt to determine the nature of the changes which take place in malt extract upon aging and the causes of said changes. I was not successful in assigning any specific composition change and therefore did not submit my results

for publication. However, as there may be some points of interest in the work done, the results are published herewith.

For many years it has been known that malt extracts, of the concentrated glycerin variety, assume a dark color very soon after manufacture, and upo aging a year or more acquire an acid taste and an od of decomposition.

The questions have been: (1) Does this char affect the diastasic power of the extract? (2) Is t change brought about by any characteristic chang the composition of the extract?

To answer the first question, samples of mal tract, the diastasic power of which had been mined at the date of manufacture, were ca selected from a series extending back twelve r and their starch hydrolyzing power again deterr

Five grams of the extract were diluted to with distilled water and thoroughly mixed of this dilution were then added to 100 cc. of cent starch paste of 40° C. and the mixture m at 40° C. until hydrolysis was complete, nc time required to completely digest the sta point of complete hydrolysis being taken at when one drop of the digested starch liquc produce the slightest trace of color when cc. of a solution containing 0.0006 g. of 0.0012 g. of potassium iodide. The result

Original assay at date of manufacture Minutes	Second assay Minutes	Age of extract	Original assay at date of manufacture Minutes	Second assay Min-
7	7	12 months	9	
9	15	12 months	9	
7	13	10 months, 15 days	7	
10	10	10 months	7	
10	10	10 months	8	
14	14	9 months	8	
7	7	7 months, 20 days	8	
8	8	7 months, 13 days	9	
9	9	7 months, 5 days	7	

All of the above extracts were and most of them had developed It is evident that the change w had not affected the diastasic, medicinal properties of the extra

The second question is not su extractive matter dissolved fr means of water and glycerin, phosphates, maltose and de peculiar principle termed diast and carbohydrates of a hig "malto-dextrine." To form nature of the changes takir of these ingredients should work I selected samples r weeks to three years.

The theory of the met haust the malt extract w this alcoholic extract the dextrose as well as other

residue from the alcoholic extract after careful drying was exhausted with distilled water and from this water extract the percentage of dextrins and albumenoids was obtained.

The apparatus used consisted of the usual Soxhlet extractor, with bulb condenser, cellulose filter about 4 inches long, sand which had been previously washed with hydrochloric acid and subsequently freed of acid, and absolute alcohol which had stood over unslaked lime while boiling 24 hours in a reflux condenser and distilled immediately before use.

Into the cellulose filter introduce about 30 grams of the dried sand: filter and sand were carefully tared upon an analytical balance and upon the sand 10 grams of the malt extract were accurately weighed. The filter with its contents was then placed in the extractor and this was in turn connected at its upper end with a bulb condenser and at its lower end with a 16 ounce distilling flask by tightly fitting rubber stoppers covered with tinfoil. The 16 ounce distilling flask contained about 10 ounces of recently redistilled absolute alcohol, and was shielded from the direct flame of a Bunsen burner by a sand bath.

The extraction of the malt extract by the absolute alcohol was continued for about 48 hours at intermittent intervals of 8 hours at a time, or until a portion of the alcohol siphoning from the malt extract failed to reduce Fehling's solution, showing that all the sugars had been extracted, and also left no weighable residue upon evaporation.

means of DeFrens' table given in Leach's "Food and Drug Inspection," pages 595 to 597. This finished the work on the alcoholic extract.

The apparatus consisting of the cellulose filter, sand, balance of the malt extract, together with the distilling flask were carefully dried; and, after drying were connected up as before, using the same quantity of distilled water as of absolute alcohol in the previous extraction.

The distillation was continued for another 48 hours at 8-hour intervals or until a portion of the water siphoning from the filter did not leave a weighable residue upon evaporation.

This constituted the second or aqueous extract. It was made up to 500 cc., thoroughly mixed and from it the following determinations were made:

1—Total solids and

2—The percentage of dextrin and albumenoids.

The total solids were obtained as in the alcoholic extract. The percentage of dextrins and albumenoids was calculated as the difference between the total solids and the per cent of ash. The other determinations made were moisture, acidity and diastasic strength.

The acidity was determined by diluting 2 grams of the original extract to 250 cc. with distilled water and titrating with $N/10$ sodium hydroxide using phenolphthalein as indicator direct, or if the solution was too dark the dropping plate was used, and the acid calculated to lactic acid. The results follow.

Age of malt extracts Months	Alcoholic Extract			Aqueous Extract			Ash	Total determined calculating from total solids	Total determined calculating from sugar	Undetermined calculated as albumenoids and diastase	Diastasic strength when manufactured Min.	Present diastasic strength Min.	Lactic acid Per cent
	Soluble in alcohol Insoluble in water Per cent	Total solids	Maltose and dextrose	Total solids	Per cent dextrin	Moisture							
32	1.82	60.51	58.85	9.3	8.42	29.26	0.88	101.77	99.23	0.77	10	45	4.5
30	0.57	53.66	52.01	13.3	12.7	31.04	2.04	100.61	98.36	1.64	10	45	4.26
24	1.84	55.68	50.27	8.86	7.19	32.34	1.67	100.39	93.25	6.75	6	9	..
23	0.65	52.53	49.64	15.34	13.50	33.37	1.84	103.73	99.00	1.00	6	10	..
17	1.16	57.50	53.36	12.37	10.87	29.16	1.5	101.69	96.05	3.95	8	13	..
8	0.71	55.82	53.54	6.25	4.52	36.00	1.73	100.51	96.50	3.50	9	9	..
1	0.65	59.96	52.62	11.11	9.06	30.47	2.05	104.24	94.85	5.15	6	6	0.09

This alcoholic extract contains all of the sugars, some coloring matters with resins from the hops and some glycerin. It was evaporated to dryness at 80° C., the residue dissolved in distilled water and the solution made up to 500 cc. with distilled water and filtered upon counterpoised filter papers.

From this solution the following determinations were made:

1—The percentage of extract soluble in alcohol but insoluble in water. This was determined by drying and weighing the contents of the filter paper above.

2—The percentage of total solids in the portion soluble in alcohol and soluble in water. This was determined by weighing 20 cc. of the solution in a tared dish, evaporating to dryness and weighing again.

3—The percentage of reducing sugars was determined gravimetrically by means of Fehling's solution, calculating the weight of reduced CuO to maltose by

CONCLUSIONS

I—Malt extract even after having changed to an almost black color and having a disagreeable taste is not necessarily inactive, and when properly made it is potent for at least one year.

II—Although the analysis of the extracts of different age did not show any definite series of changes in sugar or dextrin content, no definite conclusions could be drawn as to just what the nature of change was which took place. The results do indicate what the cause might be and further experiments have convinced me that the cause of the deterioration of the diastasic power of malt extract is due to the development of lactic acid and when the amount reaches a strength of 1 per cent or more it greatly impedes starch hydrolysis. This developed acidity also undoubtedly causes the above mentioned blackening of the extract.

LABORATORY AND PLANT

THE PYROMETER IN THE ASSAY MUFFLE[1]

By Frederic P. Dewey[2]

Standing alone, by itself, a pyrometer reading has absolutely no value as a control of assay operations in a muffle or as a guide to the assayer in carrying on such operations. The reasons for this are varied and complex. (1) The temperature that controls the success of the operation is that of the lead button undergoing oxidation. At present we have no means of learning this temperature under practical working conditions, so that some suitable place must be selected within the muffle for the location of a pyrometer. (2) Unfortunately, however, there is absolutely no approach even to a fixed relation between the pyrometer reading at any given point available and the temperature of the oxidizing button. The oxidation of the lead supplies much heat to the button, but its effect upon the pyrometer is negligible. One factor governing the amount of heat utilized by the button is the rate of oxidation of the lead, and this in turn is, within wide limits, largely influenced by the passage of the air over the button, so that to fully utilize and apply the pyrometer reading we must also know the height of the barometer and the effect of variations in the barometer readings upon the draft of the particular muffle under consideration. Further and most important, from a practical standpoint, is the freedom of entrance for the air to the muffle. In other words, by manipulating the door or the stopper of the muffle, widely varying differences between the button temperature and the pyrometer reading may be produced. The effect of the door conditions is twofold. It affects the supply of air to the button and also the actual temperature of the bottoms of the muffle on account of the varying amounts of air that have to be heated there in passing through the furnace. Finally the relation of the position of the button within the muffle to that of the pyrometer is vital. Therefore, to intelligently utilize any stated pyrometer reading it is essential to have exact information upon a variety of other conditions surrounding the operation.

Bradford[3] pointed out the inconsistencies of various statements regarding pyrometer readings in assaying and well established facts, such for instance as advising a temperature of 700° to 750° for cupellation when it requires at least 906° to fuse litharge. In a series of tests he demonstrated the large amount of heat supplied by the oxidation of the lead and the higher temperature thereby attained by the button. His arrangement of apparatus was ingenious, but risky to the pyrometer couple and not applicable to routine work. He gives an excellent description of the conditions immediately surrounding a cupellation. Fulton, Anderson, Goodner and Ossa[4] determined

the difference in temperature between an empty cupel and the cupelling lead in an adjoining cupel as 145°, and also give various other temperature determinations, under the conditions employed by them.

For a long time I have been engaged upon an investigation into the conditions surrounding the assay of gold bullion as affecting the accuracy of the results obtained. Naturally the question of the temperature of cupellation early attracted attention, but there were so many other conditions to be investigated where our information was meagre, while the temperature question seemed to be under fairly good control by the eye of experienced cupellers, that the use of the pyrometer was not actively taken up until recently.

In the early days of the investigation various points regarding temperature were carefully considered and some of the problems were worked out. Some of the problems presented themselves with emphasis. In this connection a careful distinction should be drawn between the problem of ascertaining the effect of the various conditions of the cupellation upon the temperature of the cupelling bead and the problem of the regulation and adjustment of these conditions so as to produce the best possible conditions for cupelling, and the final problem of establishing a suitable indicator or guide to show that the proper conditions are being maintained, and especially an indicator which may be applied in different muffles and under varying conditions.

In a broad and general way the time required to work off a given weight of lead is a crude indication of the temperature of the cupellation. When carrying on uniform work in quantity the decreasing size of the button is a general guide for the temperature and a rough notation of the time will often be useful in explaining irregularities of the results. If the general conditions remain uniform, a prolonged cupellation indicates lack of heat, and a rapid one an excess of heat. In making time observations it is essential to adopt some fixed point in the operations to begin taking the time and another to stop. If all the other conditions could be rigidly controlled and the time be very carefully observed, it would furnish a good guide to the temperature, but it would be available only at the finish of the run and could not be used to change conditions during the run. Also, it could not be applied at other times or places or under different conditions. Again it furnishes no preliminary evidence that the furnace is in good condition before starting the work.

It is, however, hardly ever possible to control the other conditions and sometimes accidental variations creep in. On one occasion, when the conditions, including the temperature, appeared to be normal, it became evident that the lead was not oxidizing fast enough. An examination showed that in setting a new muffle the workman had not put the slit in the back of the muffle exactly opposite the chimney outlet. This choked off the draft and retarded the oxidation. The retardation of the work was, of course, excessive, but

this experience emphasizes the natural effect of changes in the barometer upon cupellation. A resetting of the muffle corrected the difficulty.

Another *post facto* temperature indicator is the amount of gold absorbed by the cupel in gold bullion assaying, high absorption under similar conditions, indicating high temperature. Here again controlling the other conditions is difficult and I have found this indicator to be of value largely in emphasizing the fact that variations in the other conditions may falsify the pyrometer reading. It makes a difference whether the pyrometer is rising or falling. If we could hold the pyrometer at the same point for a long time before making the cupellation this cause of difference would be minimized, but this is impracticable in every-day work. It makes a difference if the muffle be new and in good condition or old and nearly worn out, and it must not be forgotten that a new muffle may be poor and leak more than an old one, which was of good quality when new.

The only feasible place to put a pyrometer in an assay muffle is close to the top of the arch of the muffle and for convenience it must be inserted from the back. We all know, of course, that closing the muffle increases the temperature and that on moving toward the back of the muffle the temperature rises, as practical every-day working facts. In order to get a more exact idea as to the difference in the temperature in different parts of the muffle and the relations between these temperatures and the fixed pyrometer readings, a second portable pyrometer was placed on the bottom of the muffle in varying relations to the fixed pyrometer as follows: directly under the fixed pyrometer, at the right side and at the left side in the same cross-section as the fixed pyrometer, close to the front in the middle and on each side of the muffle. In some of the arrangements empty cupels were placed beside the bottom pyrometer.

There are three principal causes for differences in the two pyrometer readings: position within the muffle, freedom of entrance of air to the muffle, and condition of the burners on either side of the muffle. In general, the door conditions, governing the entrance of air to the furnace, exert a powerful influence upon the temperature within the muffle, and often cause wide differences in temperature in different parts of the muffle. Under the conditions of these tests, on opening the closed muffle, either pyrometer may fall 100° or more in ten minutes, and a further 10° or 20° before becoming steady. In the closed muffle the two pyrometers registered alike in only one instance, and differed 40° in one. In every instance the movable pyrometer, on the bottom of the muffle, fell more than the fixed pyrometer, at the top of the arch, on opening the closed muffle, and in one instance 40° more.

A point of grave concern is the stability of the pyrometer. In the above tests both of the pyrometers were practically new and may be depended upon, but the effect of long use, for continuous periods, in the litharge-laden atmosphere of the muffle upon the instrument is unknown. It is known that the hot litharge fume is destructive to the tube, and it is only a question of time when it will affect the enclosed couple. At present there are no ready means for testing the accuracy of the pyrometer from time to time, and

it is difficult for an assayer to judge when it is beginning to fail.

In conclusion, I would say that, notwithstanding the objections I have described, the pyrometer occupies a useful field as a general guide to the heat conditions in the assay muffle. In the old and established practice of assaying in the Mint service, in the large laboratories, one or two men do practically all of the cupelling and they grow to be very expert in judging the heat of the muffle and the condition of the cupelling bead by the eye, but the careful and proper use of a pyrometer would often help them, while the man who cupels only intermittently will find it a good general aid. But too much dependence must not be placed upon the pyrometer, and the man who depends upon it entirely will never be a good cupeller.

BUREAU OF THE MINT
TREASURY DEPARTMENT, WASHINGTON

APPROVED BUREAU OF MINES EXPERIMENT STATION AT PITTSBURGH

Plans for the proposed $500,000 Experiment Station of the United States Bureau of Mines to be located in Pittsburgh, have been approved by the commission appointed by Congress for that purpose.

Congress, a year ago, in the Public Buildings Bill, authorized a new home for the Bureau of Mines to cost $500,000. It is now expected that Congress, in its present session, will make a specific appropriation so that construction work may begin. It is hoped that contracts may be let by July 1st and the buildings completed in the fall of 1915.

The State of Pennsylvania has appropriated $25,000 for coöperation in establishing this Experiment Station.

The group consists of three main buildings facing Forbes Street. The central building of the group, the Mining Building, will be three stories in height, flanked by two main buildings, one the Mechanical and the other the Chemical Building. In the rear of these and enclosing a court will be the Service Building. Beyond the Service Building and spanning what is known as Panther Hollow and thus connecting the Bureau of Mines Buildings with the Carnegie Schools, will be two buildings over the roofs of which will pass the roadway from Forbes Street to the Carnegie School Buildings and Schenley Park.

Between the main group and the power and fuel group will be the entrance to a series of mine shafts. One of these will be used as an elevator to carry heavy material and passengers from the lower level to the upper; another will be for tests of hoisting ropes and similar mining appliances; another will be an entrance to tunnels extending under the buildings and in which mining experiments, such as fighting mine fires, will be conducted.

The portion of Panther Hollow above the Power Buildings will be arranged as a Miners' Field, the slopes of the ravine being utilized as an amphitheatre which will accommodate 20,000 spectators who may assemble here to witness demonstrations and tests in mine rescue and first-aid.

The Mining Building will contain the administrative offices, and those of the mining force. In it will be
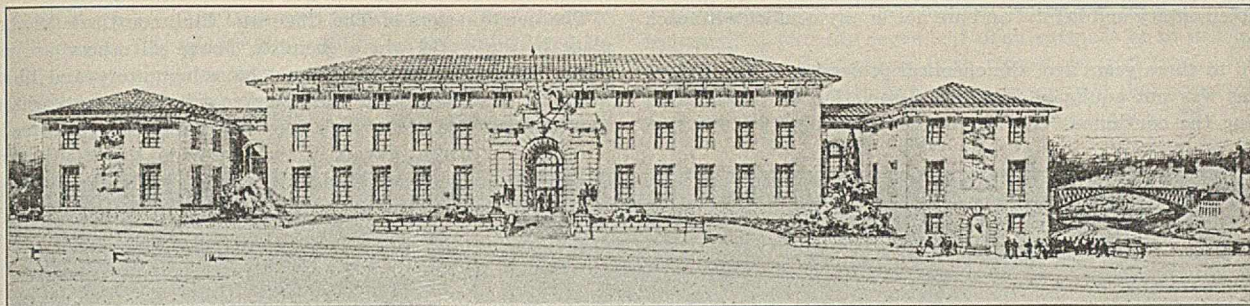
APPROVED BUREAU OF MINES EXPERIMENT STATION AT PITTSBURGH

an assembly and lecture hall, a library and smoke and other rooms for demonstrations and training in mine rescue and first-aid. The Mechanical Building will be for experiments and tests of mining machinery and appliances and the Chemical building for investigation and analyses of fuels, explosives and various mineral substances.

THE CHEMIST'S DUPLEX SLIDE RULE

By H. H. Hanson
Received February 12, 1914

In these days of efficiency and specialization, any contrivance or device which tends to save time without sacrifice of accuracy is eagerly seized upon. The slide rule has long been used by engineers. It is only within

recent years, however, that its use has been applied to chemical problems. There have been placed upon the market several so-called "Chemist's Slide Rules," but the "Duplex," invented by Dr. R. Harmon Ashley, of the University of Maine, and manufactured by the Keuffel & Esser Co., of New York, seems to be a material advance over previous rules of this kind. This rule has both the regular and the inverted scales, with the graduation incident to instruments of this kind, so that in itself it is complete, and upon it may be carried out all of the arithmetical computations which are usually required of a chemist or chemical engineer. In addition to this it carries one hundred and thirty-five chemical symbols, the acids, bases and salts being on the regular side, and oxides and elements being on the inverted side. The left index of the rule is marked "Sought," the left index of the slide is marked "Given," so that no mistake can be made in the setting it be used. With the large number of chemical symbols given almost any stoichiometric problem may be solved, as hundreds of combinations are possible with the instrument. Conversion factors are very easily and quickly obtained with one setting of the rule. The percentage composition of various compounds may be found, and problems in both gravimetric and volumetric analysis may be easily solved as described in the manual which accompanies the rule. The molecular weights of substances not inscribed on the rule are easily obtained, even though the compounds may not be given, as forty-two different elements are inscribed upon the invert side. The illustrations show the general appearance and plan of the instrument, which is very finely made and accurately marked. The graduations and symbols are inserted mechanically, thus eliminating the errors necessarily accompanying hand markings of this kind. This rule is accurate to three significant figures within a limit of error which does not exceed that of the average operation of the analytical chemist, and will be found useful for shortening operations and calculations in all branches of chemical

work. In the manual accompanying the instrument the theory of the slide rule is briefly and carefully explained, and the manner of operation is described in detail.

MAINE AGRICULTURAL EXPERIMENT STATION, ORONO

ADDRESSES

THE CHEMISTS' CLUB[1]

By WILLIAM L. DUDLEY

Almost all the professions in the United States have, in addition to their scientific associations and societies, an organization whose purpose is to foster and develop personal and professional acquaintance among the membership of that profession in a direction and to an extent not possible in strictly scientific associations. The scientific associations are not

[1] Presented at the Cincinnati Meeting of the American Chemical Society, April 6–10, 1914.

adapted to bring about this result to the greatest degree, primarily for the reason that between their meetings there is no opportunity for individuals to meet; the opportunities afforded by such scientific associations for personal intercourse are therefore intermittent and discontinuous. Continuous opportunity for such acquaintance and intercourse is offered only by those professional associations known, for short, as "clubs," which have club features as a basis, associated or combined with professional facilities and opportunities peculiar to each profession. These two classes of organizations are therefore mutually

complementary and helpful and are not in any conflict with each other.

Up to three years ago, the chemical profession in the United States was not equipped with any association or organization having the continuous club feature as an element. It is true

ENTRANCE HALL

that prior to that time The Chemists' Club, founded in 1898, with its quarters at 108 West 55th St., New York City, discharged to a greater or less extent the functions of a club, but in a manner not sufficiently continuous to meet in any satisfactory degree the needs of the chemical profession of the United States.

It was through the energy, devotion and self-sacrifice of a number of far-sighted, broad-minded and public-spirited chemists that the chemical profession, about three years ago, became possessed of quarters which contain all the elements necessary for continuous opportunity of social and professional intercourse among chemists under conditions of the usual club accommodations connected with unique and complete facilities for the conduct of professional business of all kinds under one and the same roof. To those who are engaged in the practice of industrial chemistry, such an opportunity means much. A chemist with his laboratory is not welcome as a tenant in modern high class, centrally located and well equipped buildings, and, as a result, in most of the cities, and particularly in New York, the chemist and his laboratory are crowded into the less desirable sections of the city, and then only in the less desirable buildings.

When the chemists desire to hold a meeting, they generally do so in rented quarters, poorly equipped for demonstration and experimental purposes. If a chemist desires access to chemical literature, he will find in only isolated cases a suitable library, and in still rarer instances will he find such library in charge of one who has an understanding of what chemical literature is, and what a chemist's literary needs are. If a manufacturer desires to engage a chemist for a piece of work requiring particular experience, he has, apart from The Chemists' Club, practically only the colleges and universities as a source of supply. If a chemist desires a position, he is in most cases limited to the same source of information.

The new quarters of The Chemists' Club constitute the only place in the world where chemists, above all others, are welcome, are sought as tenants and have laboratory and library facilities, under one and the same roof; where competent attendants provide them with literature, keep them informed of current events in their individual specialties, provide them with temporary laboratories, with apparatus and with chemicals, and enable them to engage help such as they may need. At the same time, they have, under the same roof, all the accommodations of a hotel, with the particular homelike features of a club, where they can always meet men of their own training and of their own line of thought; in short, once installed at The Chemists' Club, there is hardly any need of their leaving the building for anything that they might want in the way of professional or laboratory facilities, for social intercourse, for shelter or for food.

The Chemists' Club, although it is a New York corporation, and although it is located in New York City, aims to serve all the chemists and chemical industries of the entire United States, and for that purpose it has divided its membership into resident and non-resident. It is perfectly obvious what the resident members can get out of The Chemists' Club, and that what they can get is greater than what non-residents ordinarily would get, and that is why the resident member must pay larger annual dues than the non-resident.

It is clear, however, that an organization based upon national lines and doing work of a national scope must have more than local support, and in order to accomplish the greatest good must receive the widest possible support from those living outside of the resident membership area. When a non-resident member goes to New York, he can have, during his stay, all the advantages that a resident member can enjoy, and it is perfectly clear that those chemists resident outside of New York

SOCIAL ROOM

City, and who make even only occasional trips to New York, would be greatly benefited by acquiring non-resident membership and availing themselves of the Club facilities and opportunities when in New York City. Such members may very well want to have a temporary laboratory about which they can

throw all the privacy of their own laboratory. The Chemists' Club is prepared to supply this need, a service not offered by any other professional organization in the world.

As to non-resident members who never reach New York, the advantages and benefits of The Chemists' Club are perhaps
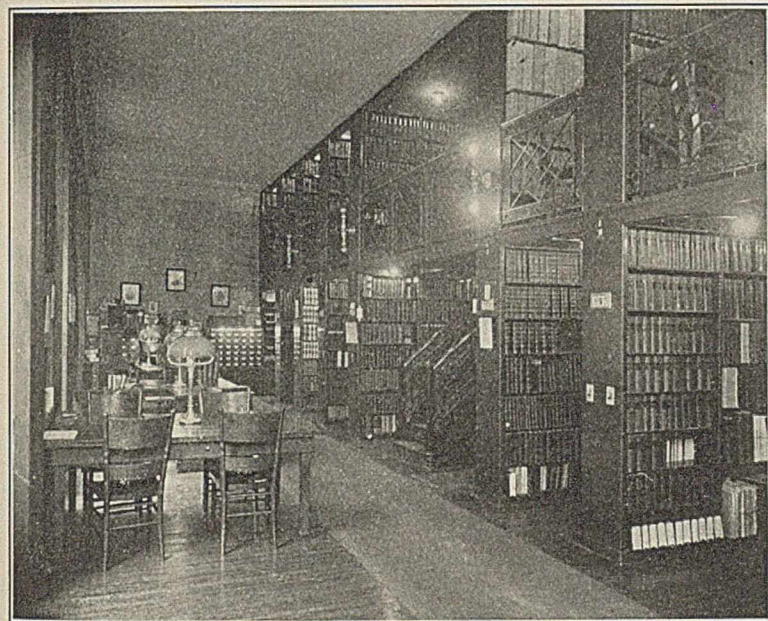
CHANDLER LIBRARY

not quite so obvious, but nevertheless valuable and certain; some day these non-resident members will want to have literature compiled or translated for them in a hurry, and at no place can it be done as well as at The Chemists' Club; or they may wish to have information as to the literature of a certain art, and that can be done no better anywhere than at The Chemists' Club; they may want to have in their hands a book not accessible at their local libraries; if such book is in duplicate in The Chemists' Club library, it is loaned to them, and if not in duplicate, a copy, photographic or otherwise, will be made and forwarded at a substantial cost; or they may want to obtain the services of a man skilled in a particular branch—the only place that they can turn to and get satisfactory information is The Chemists' Club. It may very well be that a particular non-resident member might want such service only once in two years, but if he does, whatever he has expended in the way of membership fees is undoubtedly amply repaid by the very fact that such opportunities exist and are always at his command. Preparedness and ability to do, or have done, such things is something of such great value, that beside it the annual contribution towards the realization and maintenance of such a state of affairs is wholly insignificant; each chemist must make his contribution so that these opportunities may exist when he needs them. It is merely another variation of "In time of peace prepare for war."

Coöperation is the only way in which a profession can advance, and the opportunity of coöperation necessary to the advancement of the chemical profession is offered by The Chemists' Club. Without personal contact with men of the same profession and without opportunity for such professional contact, the growth of the profession must necessarily be slow, if it does not diminish to an extent properly to be described as a standstill.

Those members of the chemical profession, and all engaged in industrial pursuits dependent upon chemists or in which the chemist plays a part, owe it to themselves and to the future of their own profession or business to see to it that opportunity for growth and development is as great as possible. The Chemists' Club offers the best opportunity for such growth and development, and it cannot reach its highest state of efficiency until every public-spirited and high-minded member of the chemical profession or industry has contributed his share to

THE MEMBERSHIP OF THE CHEMISTS' CLUB

Year	Resident, life and honorary	Non-resident and foreign	Junior	Total
1898	41	48	..	89
1899	135	56	..	191
1900	130	109	..	239
1901	143	118	..	261
1902	138	123	..	261
1903	150	134	..	284
1904	172	142	7	321
1905	164	166	11	341
1906	169	165	22	356
1907	195	161	25	381
1908	208	167	24	399
1909	225	167	19	411
1910	308	341	28	677
1911	412	524	47	983
1912	447	570	75	1092
1913	447	607	80	1134
1914	455	638	92	1185

the extent, at least, of becoming a non-resident member, and making full use of the opportunities offered.

An organization like The Chemists' Club grows with the service required of it, and with the support given it; it is to be hoped that every chemist wherever he may reside in the United States, and every person engaged in business involving chemistry, will feel that he has not done his full duty by the profession and business of chemistry until he has actively identified himself in some way or other with The Chemists' Club.

It is now three years since the new quarters at 50-52 East 41st Street, New York City, were opened, and those who have

DINING ROOM

sacrificed much time and effort in developing The Chemists' Club to its present state feel encouraged by the growth in the interest in the Club which is manifested throughout the United States.

In order that a mental picture of the growth of The Chemists' Club and its influence may be obtained, information has been collected as per table on preceding page.

LABORATORIES

Of these there are five floors and all of them rented to permanent tenants. The three "transient" or so-called "Club" laboratories, which are maintained by The Chemists' Club, have all been taken and usually there is a waiting list of satisfactory size.

LIBRARY, CLERICAL, LINGUISTIC AND LITERARY SERVICES

The library now contains 36,000 volumes, including 400 journal sets. Many of the volumes (18,000) are duplicates or triplicates and are available to members for loan purposes for which no charge is made except that necessary (25 cents) to cover cost of packing and insurance, the member paying transportation charges both ways.

The range of service rendered by the library staff includes

ENTRANCE TO AUDITORIUM

not only copies or photographs of publications or of pages thereof and translations into English from other languages, but also the collection of the literature in not only the library of The Chemists' Club but other libraries in New York City or elsewhere, if necessary; further, systematic recording of current literature in which members may be professionally and otherwise interested and for which they pay a nominal fee; searches

USERS OF THE CHEMISTS' CLUB LIBRARY

	1911	1912	1913	1914
January.............	..	124	148	346
February............	..	137	190	348
March...............	..	127	196	...
April...............	..	129	224	...
May.................	..	133	252	...
June................	82	151	257	...
July................	77	150	227	...
August..............	75	131	260	...
September...........	98	134	256	...
October.............	109	125	261	...
November...........	106	105	250	...
December...........	115	100	330	...
Average.............	95	129	238	347

of literature, patent and otherwise, on intricate and complex chemical questions as well as statistical and similar searches and compilations are undertaken.

The number of users of the library is increasing as shown in the preceding table.

The clerical, linguistic and literary service was begun in March, 1913, and the following statistics show a satisfactory and wholesome growth in the work:

1913	Translations		Subscribers to the clipping service	Searches, literary and patent
	No.	No. of words		
March............	2	2,850	4	1
April.............	3	8,010	6	6
May..............	3	37,500	8	10
June.............	6	9,540	21	14
July.............	9	15,030	22	7
August...........	5	1,325	24	7
September........	17	25,300	28	10
October..........	14	25,525	30	10
November........	9	90,800	48	7
December........	11	36,940	51	11
1914				
January..........	14	26,525	55	18
February.........	28	62,675	58	19
Total...........	121	342,020	—	120

The translations average 2,826 words each and 26,300 words per month, or 10 average translations per month. These services, *i. e.*, translations, clippings, searches and copies or photographs as well as the use of the library are available to the public and are not restricted to the membership of The Chemists' Club.

EMPLOYMENT BUREAU

This was begun in 1905. Its activities are reflected below; its use is open to all, whether members of The Chemists' Club or not:

	APPLICANTS		POSITIONS	
	Enrolled	Placed	Enrolled	Filled
1905................	60	21	28	21
1906................	80	20	51	20
1907................	351	86	108	86
1908................	582	39	64	39
1909................	220	72	120	72
1910................	245	92	217	92
1911................	...	...	...	...
1912................	464	120	216	120
1913	647	119	294	119
1914—January and February........	112	15	66	15
Total...........	2761	584	1164	584

A total of 584 positions was filled in 8 years (omitting 1911 for which figures are not available), or an average of 73 positions per year; the disparity between positions available and positions wanted, namely 2 to 5, or in numbers 1597, clearly shows the desirability of encouraging employers of chemists and of chemical assistants to make more extended use of this branch of The Chemists' Club.

RESTAURANT

In January, 1912, The Chemists' Club took over the management of the restaurant from the caterer, who had theretofore conducted it. The number of meals served for each month since is as follows:

	1912	1913	1914
January.................	901	1,482	1,898
February...............	1,162	1,522	2,245
March.................	1,577	2,051	...
April..................	1,643	1,924	...
May...................	1,483	1,631	...
June...................	1,392	1,488	...
July...................	1,352	1,540	...
August.................	1,599	1,320	...
September..............	3,930	1,328	...
October................	1,392	1,503	...
November..............	1,409	1,462	...
December..............	1,495	1,600	...
Total.................	19,335	18,851	
Monthly average.........	1,611	1,571	2,070

Many times the patronage that has so far been bestowed upon the restaurant could be satisfactorily served, without in the slightest crowding or overworking the mechanical equipment of the restaurant (which is the smallest unit that could be installed).

SLEEPING ROOMS

The information regarding these shows clearly how our non-resident membership is increasing its use of the quarters provided; the tenancy of these 18 rooms is divided into resident members and non-resident members and guests; the number of times per month that the quarters were all taken, *i. e.*, "sold out" and that members had to be sent to the "Annex" (The Murray Hill Hotel) for the night is shown in the following:

	Resident		Non-resident		Guests		Total		"Sold out"	
	1912	1913	1912	1913	1912	1913	1912	1913	1912	1913
January........	9	22	45	53	12	11	66	86	0	3
February.......	13	15	55	41	10	3	78	59	1	1
March.........	14	14	49	47	9	4	72	65	0	2
April.........	15	16	37	48	11	5	63	69	4	5
May..........	17	17	47	47	2	12	76	76	1	4
June..........	21	14	37	47	8	10	66	71	11	5
July..........	21	17	37	46	8	13	66	76	8	8
August........	21	19	28	32	2	9	51	60	3	8
September.....	14	17	37	45	4	5	55	67	7	3
October........	17	19	40	49	10	4	67	72	1	7
November......	18	18	36	45	7	6	61	69	1	2
December......	15	21	40	60	9	7	64	88	0	4
1914										
January.......	16		62		15		93		8	
February.......	16		53		8		77		4	

However, even with this encouraging showing, it is nevertheless true that The Chemists' Club itself can provide hotel accommodations to very many more than are now making use of it.

SOCIAL GATHERINGS

From January 11, 1912, to March 1, 1914, 111 private dinners or public banquets and all connected with meetings of a chemical nature were given in the quarters of The Chemists' Club; these were attended by 6539 persons.

RUMFORD HALL

This is an auditorium seating 300; is equipped with ample demonstration and experimental facilities. It is the regular meeting place of the New York Sections of The American Chemical Society, The Society of Chemical Industry and The American Electrochemical Society.

A number of social, musical and literary organizations not connected with The Chemists' Club also use Rumford Hall for their several functions.

This showing demonstrates a healthy growth in the membership of and in the interest in The Chemists' Club since it left its modest quarters at Fifty-fifth Street, where it provided merely a meeting place for the New York Sections of The American Chemical Society, The Society of Chemical Industry, The American Electrochemical Society and The Verein Deutscher Chemiker; there it had its own modest library, combined with the libraries of the American Chemical Society and the Society of Chemical Industry.

The new quarters and the new facilities are due to the initiative, the foresight, the loyal enthusiasm and abiding faith in the ultimate outcome of an enlarged Chemists' Club, on the part of its former president, the late Professor Morris Loeb. By founding The Chemists' Building Company, whose sole aim and object was to finance, build and develop a structure suitable for what was then considered as the true and full purpose of The Chemists' Club, the start was made toward an actual realization of what had long been in the mind's eye of many of the thoughtful and far-seeing chemists of the country, as a true and real and serviceable Chemists' Club.

The Chemists' Building, which is the home of The Chemists' Club, is an eleven story fire-proof structure, centrally located in New York City and having a 56-foot frontage. The structure put up and the facilities provided are on the smallest scale that could reasonably be regarded as being efficient. Nevertheless, the total investment of The Chemists' Building Company in the building occupied to the extent of 50 per cent of its available renting space by The Chemists' Club is appraised at $440,000 for taxation purposes. Practically all the stock of The Chemists' Building Company is sold, and fully paid up, and is held wholly by members of the chemical profession and business. The capital stock was taken by 171 subscribers; 139 subscribers domiciled in the resident membership area took seven-eighths of the capital stock and 32 subscribers domiciled in the non-resident membership took the remaining one-eighth.

Some of the stockholders, following the example of the late Professor Loeb, have cancelled their stock, or transferred it to The Chemists' Club. The issued stock calls for a cumulative 3 per cent dividend; no dividend has yet been paid nor are the stockholders insisting upon such payment. This magnanimous and generous action on the part of the stockholders is bringing nearer and nearer the day of a complete realization of what was planned by the Founders of The Chemists' Building Company and it is confidently expected that these dividend obligations, for which The Chemists' Club is in the final analysis wholly responsible, will be ultimately fully discharged.

The Club itself represents an investment over $60,000 in library and equipment, thus bringing the total financial investment in this enterprise up to more than $500,000.

However gratifying the growth shown in the foregoing may be to those who have given the best of their efforts, time and thought to the realization of The Chemists' Club, yet it is perfectly clear that the members of the chemical profession generally have not made a contribution toward the continuance and maintenance of The Chemists' Club commensurate with the benefits derived or to be derived from it, nor can it be truthfully said to be even proportional to the effort and energy contributed towards it by the Founders of The Chemists' Building Company.

VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE

CHEMICAL ABSTRACTING

By JOHN J. MILLER
Received March 19, 1914

At various times and places during the last few years the question of international coöperation in chemical abstracting has been promulgated and has brought forth some comment. So far as we know, however, no comprehensive data concerning this subject have been gathered other than those recently published in *Scienca Gazeto*, the official organ of the International Esperanto Scientific Association. The appearance therein of an article giving the membership of the German, French, London and American societies, the costs of the abstract journals per member, pages of abstracts, etc., prompted an investigation of the figures given and finally the writing of this article.

Table I gives the data (for 1911) printed in the above mentioned periodical and Table II the results of our calculations:

TABLE I

	No. members	Total cost	Cost per member	Total No. of pages	Total No. of abstracts	Pages per abstract	Abstracts from other journals	Abstracts of patents
Chemical Abstracts..	5,603	$31,557.00	$5.65	4,741	20,916	0.17	1,542	5,179
J. Chem. Soc.......	3,132	13,031.00	4.15	2,586	5,159	0.41	169	161
Chem. Zentr.	3,352	14,706.00	4.40	4,422	9,231	0.39	17	1,097
Bull. soc. chim. Fr..	1,024	7,159.50	7.00	2,291	4,073	0.43		
Total.....	13,111	66,453.50		14,040	39,379		1,728	6,437

The great discrepancies are due to various errors in Table I. For example, for the *Journal of the Chemical Society* no editorial expense seems to have been considered. For *Chemisches Zentralblatt* the total membership of the German Society is

used instead of the number of subscribers to *Chemisches Zentralblatt*. In our calculations three-fourths of the salaries of the editors of the *Journal of the Chemical Society* have been counted as abstract expense and the same is true of the *Journal of the Society of Chemical Industry*. Less than one-half of the pages of the *Journal of the Chemical Society* is taken up with original communications, so we figure that because of their complete index and the attention of the editors naturally required for abstract work as compared with journal work, three-fourths of the editors' energy and time is given to the abstract part of the periodical. Only one-fourth of the *Journal of the Society of Chemical Industry* is original material, wherefore it seems proper to consider three-fourths of the editorial expense as due to work on the abstract section.

Table II portrays a number of interesting facts, among which may be mentioned: (1) *Chemical Abstracts* is the largest (in number of abstracts) chemical abstract journal in the world;

evident that no foreign abstract journal can lay claim to completeness even if the field of patents be excluded. The question arises, however, as to whether *Chemical Abstracts* in its effort to abstract all chemical material is including too much material that is only of indirect chemical interest. This is a subject which has often been discussed by the editors and abstractors of *Chemical Abstracts* but invariably the verdict has been that our journal is not too comprehensive. The editors realize the danger of including too much material and are persistently struggling against error in this regard. Even a hasty examination of the other abstract journals will show that some of them print abstracts which we would exclude on non-chemical grounds or because of their news-item nature. The *Journal of the Society of Chemical Industry* prints industrial reports which we would like to include but cannot because of lack of funds. Such a study might suggest that if these other abstract publications were to follow their present rules as to desirability for abstracting

TABLE II

	Sub- scribers	Total cost	Cost per member	Total pages	Cost per page per member	Cost per page	Number of abstracts	Cost per abstract
Chem. Zentr., 1909 II, 1910 I[a]	1,542	$21,027.67	$13.64	4,364	$0.003	$ 4.82	10,542	$1.99
J. S. C. I., 1912	4,198	23,593.80	5.62	971	{ 0.0057 ÷ 2 = 0.0028	24.30 ÷ 2 = 12.15	} 7,200	3.28
J. C. Soc., 1912	3,248	16,338.20	5.03	2,648	0.00189	6.17	5,833	2.80
Chem. Ab., 1912	6,219	32,596.00	5.24	3,544	0.00147	9.197	22,659	1.438
Chem. Ab., 1913	6,673	37,258.00	5.58	4,096	0.00136	9.09	25,971	1.434

(a) No later figures are available.

(2) it costs less either on a basis of per page per member or per abstract than any other journal. Credit has been given for the fact that the pages of the *Journal of the Society of Chemical Industry* contain a little over twice as much material as those of *Chemical Abstracts*. In the *Scienca Gazeto* article the basis of comparison is the cost per member and in Table II this same comparison is made, but obviously such a basis is not the fairest possible because of the great difference in amounts of material furnished the subscribers of the various journals. Neither do we think the cost per abstract to be the best test of efficiency, because the shortest abstracts will be the cheapest and probably not the most satisfactory. The only comparison that seems worth while is the one based on the cost per page per member and therefore we wish to lay emphasis on the figures given in Column 5 of Table II.

Column 6 indicates that increase in membership means nearly a proportional increase in cost per page if the number of

TABLE III

	No. of journals abstracted	No. of abstracts, including patents	No of abstracts, excluding patents
Chem. Zentr	161 (1913)	10,862 (1913)	9,948
J. Chem. Soc	140 (1911)	5,833 (1912)	Very few patents
J. S. Chem. Ind	151 (1913)	7,200 (1912)	2,400
Z. angew. Chem	110 (1913)	5,200 (1912)	3,412
Chem. Ztg	....	13,792 (1913)	9,607
Chemical Abstracts	633 (1913)	25,971 (1913)	19,025

pages printed is kept constant, and this is true because of the printing factor; *e. g.*, if we should print 3,000 pages and had 3,500 members our printing and distribution (not counting postage) cost would be $3.12 per page. On keeping the pages constant and increasing the subscribers to 4,000, 5,000, 6,000, 10,000 our per page costs, according to our recent printing contract, would be respectively, $3.32, $3.72, $4.09, $5.71.

Table III reveals perhaps more than anything else the completeness with which the field of chemistry is covered by the various abstract journals.

The number of journals in each case is taken from the printed list attached to the index of the year indicated. It is perhaps

of articles in all of our 633 journals, the articles abstracted by all of them would exceed ours in number.

In another way a most interesting comparison can be made between four of the abstract journals, namely, *Journal of the Society of Chemical Industry*, *Chemisches Zentralblatt*, *Journal of the Chemical Society* and *Chemical Abstracts*. For example, it may be of importance to know what class of chemical articles is abstracted by *Chemical Abstracts* and omitted by the others.

We regret that it has been impossible to obtain the same data for *Zeitschrift für angewandte Chemie* and *Chemiker Zeitung*, but it would be considerable trouble so to do and perhaps is hardly necessary. Through constant reference to these three journals it has been observed that their abstracts are mainly of articles of an industrial nature. *Chemisches Zentralblatt* and the *Journal of the Chemical Society* confine their work largely to pure science, whereas *Chemical Abstracts* covers both branches of chemistry. But in order to determine whether *Chemisches Zentralblatt* and *Journal of the Chemical Society* are complete even in abstracts of pure chemistry we need only to note the figures in the third and fourth columns of Table IV, in the departments of General and Physical Chemistry, Electrochemistry, Analytical Chemistry, Mineralogical and Geological and Biological Chemistry. As to the reverse of this query, that is to say, is *Chemical Abstracts* missing articles abstracted in these other journals, we would say that such an interrogation is proper and important. The answer is that the abstract part of every issue of the following journals is checked shortly after arrival at this office and that any article (of a chemical nature) which has been overlooked is assigned for abstracting (from the original if possible): *Chemisches Zentralblatt, Journal of the Chemical Society, Journal of the Society of Chemical Industry, Chemiker Zeitung, Experiment Station Record, Bulletin of Agricultural Intelligence and Plant Diseases, Neues Jahrbuch* and *Stahl und Eisen*. Other abstract journals are watched by various abstractors so there is little danger of missing an article of value.

The facts so far given are likely to suggest even to the casual observer that much of this abstracting work is a matter of duplication and that some step should be taken to bring about a more economical abstracting system. With this we agree,

TABLE IV

	No. of abstracts in one issue of C. A.	No. not found anywhere in		
		J. S. C. I.	Chem. Zentr.	J. C. Soc.
Apparatus...........	20	18	9	13
Gen. and Phys.......	61	56	12	24
Radioactivity........	20	20	8	14
Electrochem.........	32	30	27	32
Inorg. Chem.........	19	14	2	4
Analyt. Chem........	33	20	14	14
Min. and Geol.......	6	5	5	2
Met. and Metallog....	85	61	60	70
Organic.............	84	73	5	Have nearly all
Biological...........	232	Missed almost all	166	..
Biological(a)	209	..	145	..
Biological(a)	315	..	..	240
Foods...............	20	19	8	16
Water...............	23	22	16	18
Soils and Fertilizers..	21	19	8	14
Ferm. and Dist. Liq...	28	23	6	22
Pharmaceutical......	26	25	9	23
Acids...............	4	4	3	4
Glass and Ceramics....	17	16	16	16
Cement.............	20	20	18	20
Fuels...............	31	28	25	27
Petroleum...........	20	18	14	18
Cellulose...........	3	1	1	2
Explosives..........	7	5	3	7
Explosives(a)	19	..	14	..
Dyes and Textiles....	15	10	10	14
Pigments, Rubber, etc.	1	1	1	1
Fats.................	8	..	2	6
Fats(a).............	17	13	..	..
Sugar...............	2	..	2	2
Sugar(a)............	21	10	16	..
Leather.............	2	..	1	2
Leather(a)	8	..	3	..
Leather(a)	18	14	..	..

(a) In order to obtain representative figures these departments were checked in more than one number of *Chemical Abstracts*.

but before further discussion desire to submit the facts given in Table V.

That there is duplication in abstracting in all of these countries is immediately evident and that this condition is most serious in Germany is also clear. The size, scope and value of the above-mentioned German journals are such as to make

TABLE V—CHEMICAL ABSTRACT JOURNALS OF THE WORLD

GERMANY

Chemisches Zentralblatt.
Chemiker-Zeitung.
Zeitschrift fuer angewandte Chemie.
Zentralblatt fuer Biochemie und Biophysik.
Biedermanns Zentralblatt fuer Agrikultur-chemie.
Neues Jahrbuch fuer Mineralogie.
Zeitschrift fuer Untersuchung der Nahrungs- und Genussmittel.

FRANCE

Bulletin de la société chimique de France.
Le Mois scientifique et industriel.
Revue de metallurgie.

ENGLAND

Journal of the Chemical Society.
Journal of the Society of Chemical Industry.

UNITED STATES

Chemical Abstracts

coöperation between *Chemisches Zentralblatt* and foreign abstract journals only an initial step. Effective combination would necessarily include most of these other German journals. In France the *Bulletin de la société chimique* has fairly important industrial competitors in the *Le mois scientifique et industriel* and *Revue de metallurgie*. In England the field is about evenly divided. In the United States the *Experiment Station Record*

and *Science Abstracts* are so limited in scope as not to encroach upon the province of *Chemical Abstracts*.

The two propositions relative to abstracting recently suggested by an International Commission are (1) the publication of an International Journal of Abstracts in three languages; (2) the publication of three editions of an International Journal of Abstracts, viz., in English, French and German.

No. 1 doubtless means that the abstracts should appear in the language of the original article when that language is English, French or German. Probably all other languages would be translated into German because the majority of chemical articles are printed in German. (According to statistics in *Scienca Gazeto* 50 per cent of all chemical articles are in German, 13 per cent in French, 27 per cent in English, and the remainder or 10 per cent in Italian, Russian, etc.) This is the method of the *Botanisches Centralblatt*, which is a rather small journal and has comparatively few readers in this country. It has been estimated by one of the professors of botany at Ohio State University that not more than 300 men in this country make consistent use of this journal and that those who do are research men who can probably read French and German readily. When we consider that there are now about 6700 American subscribers to *Chemical Abstracts* and that perhaps the same number of English chemists are taking an abstract journal (in 1912 the membership of the Chemical Society of London was 3,248 and of the Society of Chemical Industry 4,198) there is some objection to their being required to read 60 per cent of their abstracts in German and 13 per cent in French. The cost of *Chemical Abstracts* to each member of the American Chemical Society was, in 1912, $5.24. Assuming that there was an international abstract journal (taking the place of *Chemical Abstracts*) published in accordance with plan No. 1, it would need to contain about 25,000 abstracts, of which 15,000 would be in German and 3,250 in French. Almost any of us would rather pay our $5.24 and have our abstracts in English. The time lost in translating on the part of Americans and Englishmen might involve such an economic loss as to eliminate any possibility of saving due to coöperation in an abstract journal of this kind. But our international journal would approach so nearly in cost per member our $5.24 that we would be required to do all this reading of foreign languages for almost nothing. The *Scienca Gazeto* figures that an international journal would cost one-third less per subscriber than *Chemical Abstracts* is now costing the members of the American Chemical Society, which would be equivalent to receiving $1.78 per year for this extra work. We cannot but conclude that Dr. W. A. Noyes satisfied a great need and performed a valuable service to American chemistry when he established an American abstract journal.

But whether a saving of $1.78 per member is possible is still a question. It is more in the nature of a good guess, we believe, than of a calculation. In going over our printing bills for 1913 and refiguring them on the basis of an abstract journal of the same size as *Chemical Abstracts* to be sent in lieu of the *Journal of the Chemical Society, Journal of the Society of Chemical Industry, Chemical Abstracts, Bulletin de la société chimique de France*, and *Chemiches Zentralblatt* we obtain as the total cost of printing and wrapping $45,247. The number of copies needed would be 18,600 (see Table VI).

Since Table VI shows that the printing cost of an abstract journal is about 60 per cent of the total cost, this would give as the total cost of an international journal about $75,000 and we have not considered the fact that the sending of the copies from Germany (it would probably be printed in Germany) to other countries would cost in postage about $2,800 per year more than at present. This would make the total $77,800 per year. The abstract journal would then cost each member $4.18 per year instead of $5.24, and still two-thirds

of it would be in a foreign language. If the printing cost is 66 per cent of the total cost, the cost per member would be $3.83.

<div align="center">TABLE VI</div>

	Total cost	Printing and distribution cost	Per cent of total cost.
Chemical Abstracts........	$32,596	$19,562	60
J. Chem. Soc............	16,338	10,613	65
J. Soc. Chem. Ind........	$23,593	15,606	66
Chem. Zentr.............	21,027	11,784	52
			—
		Average,	61

But there remain several factors which have not been taken into consideration: (1) A movement of this sort would surely reduce the memberships of the various societies and thus raise the cost above the figures given. There are hundreds of members in the American Chemical Society alone who would not subscribe for a "mixed language" journal. (2) The discontinuance of *Chemical Abstracts* would necessarily mean an increase in cost of the *Journal of the American Chemical Society* and *Journal of Industrial and Engineering Chemistry* and other journals of which the abstracts are a part. (3) A part of the benefit of having an American abstract journal is that it helps financially almost 300 abstractors, makes them more familiar with the literature than they would otherwise be and keeps up interest in the Society. (4) American chemists (especially industrial chemists) seem to require abstracts from an American point of view and because of the different character of the chemical industries in the various countries doubtless the same requirement arises on the part of foreign chemists. This, Charles Baskerville has aptly stated: "I realize that it may be more desirable for us to write our own abstracts absolutely independently, inasmuch as we have our national way of looking at things." For this reason alone independent national abstract journals might spring up and compete successfully with an international periodical. (5) The above estimate of $77,800 is made on the basis of 0.17 page as the average length of an abstract. The average length of an abstract for *Chemisches Zentralblatt* is 0.39 page, for the *Journal of the Chemical Society* 0.41, and the *Bulletin de la société chimique de France* 0.43. Using 0.35 page as the proper length of an abstract (for the other societies would doubtless not be satisfied with less; they would probably object to the conciseness of style and the abbreviations necessary in *C. A.* and would desire more detail), this would mean an increase in size of the abstract journal of 100 per cent over that which would cost $77,800. If it is argued that the *Journal of the Chemical Society* and *Bulletin de la société chimique de France* have less material on a page than *Chemical Abstracts*, it should be remembered that *Chemical Abstracts* is printed in a style and size of type which makes the cost lower and that the $77,800 estimate is based on the *Chemical Abstracts* type. An increase of 100 per cent in space would raise the printing bill to $76,343 instead of $45,247. To this must be added another $2,800 postage to foreign countries, making $79,143. But this is only printing and distribution expense. The addition of $29,753 which we previously figured as abstracting, salaries and other expense (and which would be considerably too small for the proposed international journal) would bring the total cost of an International Abstract Journal similar to *Chemical Abstracts* to $108,896. If it were only $100,000, the cost per member, provided there was no falling off in members, would be $5.37. The cost to American chemists was in 1912 $5.24.

It is evident from the foregoing that, disregarding the question of the desirability of an international abstract journal and confining ourselves to the economic phase only, the proposition in accordance with plan No. 1 is not attractive. May we suggest to its advocates that they should begin their discussions concerning it with a consideration of the scope of the proposed journal and the average length of its abstracts?

Plan No. 2 contemplates the publication of English, German and French editions of an international abstract journal. In discussing plan No. 1 we gave all possible advantage to the co-operation idea by assuming that the subscription list would be the combined subscription lists of the present journals, or 18,600. It will be best to note, however, that there are perhaps 1200 subscribers to the *Journal of the Society of Chemical Industry* in this country who also take *Chemical Abstracts*, and the duplication of purchasers of the *Journal of the Chemical Society* and *Journal of the Society of Chemical Industry* will probably amount to 2,000. Therefore we believe it fair to say that the subscribers to the international journal would number in the United States 5,000 and in England 5,000 (instead of more than 7,000). Such a comprehensive abstract journal in the German language ought to raise the German subscription to 3,000 and the French to 1,100, making a total of 14,100 subscribers or members of the international association. But again the question of scope of the journal and length of abstract is of paramount importance. If the average journal is to be as complete as *Chemical Abstracts*, it will cost: for printing the English edition about $42,202; for the German edition about $21,379; and for the French $15,687; on the basis of 0.35 page per abstract. Using the same low figures as before for editing, etc., and adding to abstracting cost $4,000 for translating abstracts into three languages, the cost of the entire journal per member per year for the members of the international association would be $8.26. If American chemists are to profit financially from any such coöperation it will have to be through retrogression in regard to completeness of the abstract journal, which is surely not desirable. In order to hold the cost to the figures given, however, the other societies would have to permit the extensive use of formulas and abbreviations such as are now used in *Chemical Abstracts*. This is a question which must be settled before accurate costs under either of these plans can be ascertained.

But there are other objections to plans Nos. 1 and 2, in that both require the collecting of the copy at one office and redistribution of the printed material from that point. Aside from the excess postage cost there is the disadvantage of delay involved. For example, now we can abstract American journals within a few days of publication and have the abstracts to our members in a few weeks. The Germans can do likewise with their periodicals, and so can the French. Under the proposed scheme Americans or Englishmen could not receive abstracts from their respective journals until the trip to Europe and back had been made and under plan No. 2 these American and English abstracts would necessarily remain in the central office until translated. All abstracts would under plan No. 2 have to be held up until translations were made and then printed simultaneously with the translations.

There seems to be a point at which centralization becomes a nuisance and we believe this point is reached when we try to cross the language line or span the ocean.

The Esperanto idea will not be discussed in detail for two reasons: (1) We are told that Esperanto is not flexible enough to meet the demands of chemistry. (2) If there is to be a unification of languages for chemists throughout the world, the place to start the same would best be in the college or university, then print all chemical journals in the one language and finally use this language in the abstract journals. Unless all the chemical periodicals are printed in the one language, it means simply the learning of a new language for the sake of reading the abstract journal. And for what end? There might be a saving of $1 or $2 per year per chemist by issuing only one journal, but economy is not the goal of life.

In our opinion the solution of this problem lies in letting each society do as it sees fit about the abstracting question. It would not be right to force a member of the London Chemical

Society to subscribe more to an international journal than he is now paying for the *Journal of the Chemical Society* abstracts just because the American chemists will not be satisfied with an incomplete abstract journal or because the Germans want longer abstracts. Each of the leading abstract journals is superior in some respects to the others and is subscribed to by those to whom this superiority appeals. Each phase of the abstracting is emphasized in some one of these journals so a chemist has his choice and gets what he wants at a less cost than if all abstracts were reduced to a dead level and he had to buy everything that anyone else might desire.

The proposition that appeals to us more than anything is suggested by an announcement in the *Proceedings of the London Chemical Society* to the effect that representatives of the *Journal of the Chemical Society* and the *Journal of the Society of Chemical Industry* were to meet to discuss coöperation in England alone. This is feasible because of the unity of language and land. And for the same reason, if *Chemisches Zentralblatt, Chemiker Zeitung, Zeitschrift für angewandte Chemie* and other German abstract journals should combine there would be greater economy and greater satisfaction than in any possible kind of international journal. In France the *Bulletin de la société chimique de France* might combine with *Le mois scientifique et industriel*.

In closing we would suggest that there is a possibility of saving a little abstracting expense for each abstract journal and that broader coöperation to that extent may be practicable. It could best be attained by having the abstract journals exchange, without charge, their corrected page proofs. Then if there is any advantage in copying or translating abstracts instead of taking the abstracts from the originals, the practice could be followed to that extent. There would be nothing compulsory about it, and any practice which proved unprofitable could be discontinued summarily and without confusion. It would mean coöperation whenever coöperation is beneficial; at no other time is it desirable.

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THE PRESENT STATE OF THE CYANAMID INDUSTRY[1]

By E. J. Pranke

Cyanamid is a dry, grayish black pulverized material, which is made by combining pure atmospheric nitrogen with calcium carbide at a temperature of 1100 to 1200° C. Its principal use in this country is as a source of nitrogen in mixed fertilizers.

Fertilizers have an intimate relation to the cost of living that should be more generally recognized. It is a well known fact that the cost of living has increased in this country at a much more rapid rate than it has abroad. When we consider the facts closely, we find that the extraordinary increase in this country has been in the cost of food products, while other than foods have increased at only the general rate prevailing throughout the world. From 1900 to 1910, for instance, all commodities in this country increased in cost about 26 per cent, as compared with 9 per cent in England, and 12 per cent in France, or 15 per cent in the world, including the United States. But other than foods in this country increased only 17 per cent, while foods increased 35 per cent, or more than twice as much. While population increased 21 per cent in the ten years, crop production increased only 10 per cent.

The rapid increase in the cost of foods in this country must be checked by increased crop production, just as food prices are held down in the more densely populated European countries; the yields per acre must be increased. In Europe the yields of the staple crops average from 50 to 100 per cent larger per acre than in this country. Crop rotation, seed selection, and thor-

ough cultivation are estimated to be responsible for one-half the increased yields, while the use of fertilizers is considered, by competent authorities, to cause as much increase as all other factors put together. The countries of highest agricultural development are the largest consumers of fertilizers. Germany, for instance, spends as much money per annum for fertilizers as we do, although she has only $1/13$ of the acreage under cultivation that we have. This, moreover, is in a country of abundant cheap farm labor, which would indicate that mere muscle cannot take the place of plant food in the growing of crops.

The development of an increased use of fertilizers in this country is mostly a matter of education of the farmer, and to some extent a matter of fertilizer prices. The farmer must be taught that there is a right way and a wrong way to buy and use fertilizers, and that the right way is profitable; the wrong way may or may not be. A lower price, however, will always make it easier to earn a profit, and the lower the price the larger the profit, the greater the incentive to use fertilizers, and the larger the crops produced. Hence, any improvement in the art of manufacturing fertilizers or fertilizer materials that will make them cheaper, will ultimately lower the cost of foods, and hence, the cost of living.

Any considerable reduction in the cost of fertilizers is hardly to be expected, however, unless it takes place through a reduction in the cost of the most expensive ingredient, nitrogen. The price of phosphoric acid is now probably about as low as it will ever be. The main source of this ingredient, namely, phosphate rock, is found in enormous deposits that will last a great many years. The present method of treatment would seem to be about as economical as any that is likely to be devised. So with potash. Practically all of our potash is imported from Germany, where it occurs in great natural beds that will last for many thousands of years at the present rate of development. It is true that lately there has been considerable talk of obtaining potash by the incineration of a sea-weed, known as kelp, found in abundance on the Pacific coast. Whether potash from this source can be produced and shipped to the Eastern part of the United States at a much lower cost than the German potash can be delivered remains to be seen. A pound of nitrogen costs about four times as much as a pound of phosphoric acid or a pound of potash. The cost of the nitrogen in the average fertilizer makes up about 45 per cent of the total cost. The higher price paid for nitrogen, however, is justified by the fact that this is the element usually most needed to increase the productivity of the average soil, and moreover, its application seems to be in most cases a prerequisite for the effective utilization of the other ingredients, phosphoric acid and potash. A typical instance is found in the results of 55 years of continuous experiments on wheat in England, at the Rothamsted Experiment Station. These are as follows:

Fertilizer	Per Acre	
	Yield	Increase
None	12.9 bu.	....
Phosphate and potash only	14.8 bu.	1.9 bu.
Nitrogen only	20.5 bu.	7.6 bu.
Nitrogen, phosphate and potash	31.6 bu.	18.7 bu.

Fertilizer nitrogen may be classified according to its sources, into organic, derived from animal or vegetable matter, and inorganic, derived from mineral sources. The price of the organic ammoniates, chief of which are cottonseed meal, tankage, dried blood and dried fish, is steadily tending upward. This is due principally to the decreased per capita production of animal and vegetable products in recent years, and to the increased uses to which by-products are applied. Recently, the above by-products were used mostly in fertilizers, now they are used to a considerable extent in stock foods. The inorganic ammoniates, chief of which are sodium nitrate, ammonium sulfate and cyanamid, have lately been suffering a general decline in

[1] Presented before the Nashville, Tenn., Section of the A. C. S., February 20, 1914.

prices. The general price level of this class of nitrogen is about the same as it was ten years ago, in spite of the increase of about 26 per cent in the cost of all commodities in that time. The lower prices now prevailing are undoubtedly due to the rapidly increasing production of inorganic ammoniates. Probably the most important single factor in this movement is the production of cyanamid.

In this country the demand for cyanamid has kept pace with the supply at the current prices for inorganic ammoniates, and sometimes at higher prices. Yet, this fact has led some of those who stand in the position of advisors to the farmer to assert that they cannot recommend a new material until its advantages have been proved superior, and in addition its prices made lower than that of the older ammoniates. They overlook the fact that no industry in the early stages of its development has turned out as perfect a product at as low prices as was later found possible. Pioneering is always costly, and a pioneer industry must have the support of the public from the start in order to develop at all. It is the history of great manufacturing enterprises that where the support of the public has been accorded, the final benefits to the public are out of all proportion to what could have been expected in the beginning. The only question that broadminded men should ask, is: Has the process inherent merit? Will it prove to be a great public good? With regard to the cyanamid process the answer must be: Yes. The cyanamid process is probably the cheapest known process for producing a commercial nitrogen compound on a large scale. It is only a question of time until an ideal product is developed, and sold at the lowest prices. In the meantime, however, the industry must have the support of the public. Fortunately, it has this support now, as is evident from a glance at the statistics.

In 1904 the world's production of cyanamid was 5,000 tons. In 1909 it was 50,000 tons. In 1914 it will be 275,000 tons. The American Cyanamid Company began operations at Niagara Falls in January, 1910, with a capacity of 12,000 tons per annum. This was increased in 1913 to 32,000 tons per annum. Further extensions, which will reach completion in April, 1914, will make the yearly capacity of the American plant 64,000 tons. The world's output of cyanamid brings at wholesale prices about $14,000,000 per annum, the European product being of somewhat higher nitrogen content than the American.

Now if one were to turn to the literature on cyanamid, and on the basis of what he reads there, hazard an opinion as to the rate of growth of the industry in the past ten years, he would probably fall far short of the truth in his estimate. If the literature were taken by the public as the sole basis of judgment of the value of cyanamid as a fertilizer, it is doubtful whether there would be enough cyanamid sold to keep one small factory busy furnishing the world's supply, instead of the fourteen large factories with their output of fourteen million dollars worth of product per annum. It is conceivable that a small amount of an inferior material might be disposed of by clever salesmen for one or two seasons, but the fact of such steady rapid growth as the cyanamid industry has made is inconsistent with essential inferiority. The fact is, that the great majority of limitations that have been attributed to cyanamid simply have no bearing upon the practical use of the material. Some of the limitations mentioned in the literature do not exist at all, while the practical significance of others is found, on examination, to approach zero in value.

Advancement in the knowledge of a substance begins when its properties are expressed quantitatively. Practically all of the problems of the early days of the cyanamid industry have been solved by paying attention to the quantities involved. Let us now consider some of the characteristics of cyanamid that have been claimed in the literature to be disadvantageous, and let us note in each instance how the supposed difficulty was solved.

CALCIUM CARBIDE

This substance was occasionally found to the extent of several per cent in the material produced in the earlier days of the industry abroad. It is now entirely removed in the course of manufacture by the addition of sufficient water to entirely decompose it. The American practice of hydration makes the presence of undecomposed carbide impossible. In Europe, the last step before shipping the material is to test for carbide.

CHANGE IN WEIGHT AND SUPPOSED LOSS OF NITROGEN IN STORAGE

On exposure to the air, cyanamid absorbs moisture and carbon dioxide, which makes it weigh more. As the total weight increases, the percentage of nitrogen will of course decrease. The new weight, however, multiplied by the new percentage of nitrogen will show the same number of pounds of nitrogen present after storage as there was at the beginning. Early observers noted the decrease in nitrogen analysis, but failed to take account of the increase in weight; hence they reported large losses of nitrogen. All attempts, however, to show a loss of nitrogen in goods stored in factories have failed, when the final weight of the pile was determined, as well as the analysis of a sample drawn in a uniform manner from all parts of the pile. When storage is desirable and necessary, it is a relatively simple operation to draw a practical average sample for analysis at the conclusion of the period of storage. It should be mentioned here too that other fertilizer materials are by no means perfect in respect to their storing qualities. The practical man, however, does not ask for perfection; it is usually too difficult of attainment, and too costly and often quite useless. All that is required is that a thing be good enough for the purpose.

It is true that laboratory experiments have shown that when a few grams of cyanamid are exposed in a thin layer to a constantly saturated atmosphere of moisture for a long time an odor of ammonia is given off, and a loss amounting to about 0.02 per cent of the total nitrogen for each 1 per cent gain in weight of the exposed sample can be detected after allowing for the increase in weight. It is doubtful, however, whether this has any practical significance. The fact that iron filings will rust over night in a damp atmosphere does not prevent the use of iron for building bridges or other structures exposed to damp weather. The fact that iron filings are readily burned by dropping them through the flame of a match has not prevented the use of iron as a non-combustible building material. Even assuming that the severe conditions of the laboratory experiment with cyanamid could be applied to conditions of factory storage, the loss of nitrogen would be insignificant. In factory storage cyanamid gains in weight on an average only about 1 per cent a month. Hence a material containing 16 units of nitrogen would contain, after one month, somewhere between 15.997 and 16.000 units. To the practical fertilizer man such differences are inappreciable. Even in one year, at this rate, the loss would be only 0.036 unit of nitrogen. The best fertilizer analyses for nitrogen, however, have no meaning within 0.100 per cent, and sometimes 0.200 per cent. As a matter of fact the immaterial loss of actual nitrogen from cyanamid is probably much less than the actual losses known to occur in the decomposition of organic fertilizer materials in storage. All these are so insignificant that nobody pays any attention to them.

DUST

Attention has often been called to the dustiness of the powdered cyanamid, and to its caustic action on the skin and mucous membranes. In some fertilizer factories loosely constructed elevators and mixing machines, and open screens permit the escape of the fine material, which settles on the exposed parts of the laborer's body. If then the laborer fails to wash the dust off at the conclusion of the day's work, the lime compounds will absorb moisture and probably some of the natural oils from the skin, and cause some irritation. If, however, the laborer will

rub any kind of oil or grease on the exposed parts of his body before he commences work, and will use oil or grease again at the conclusion of the day's work, he will find that the dust will not burn during the day, and is very easily wiped off when he is through with his work. Of course the dust must be removed from the skin at least once a day. Laborers who work in the factories where cyanamid is made never have skin irritation. They take the simple precautions that have just been described.

It is a peculiar fact that when alcohol is taken the into body after one has breathed cyanamid dust, there follows within a few minutes a reaction colloquially known as a "flush." This is characterized by an increased flow of blood to the skin of the upper part of the body, deepening its color, and giving a suggestion of swelling. The subject also has a feeling of oppression in his breathing. In no case has anyone ever been known to suffer harm from a "flush," but only temporary discomfort, the degree depending upon the amount of alcohol imbibed. The effects usually pass away within an hour after taking the alcohol. Moreover, alcohol is the only known cause of this effect of breathing the dust. Total abstainers never experience the "flush."

In the better equipped fertilizer factories, the machinery is enclosed in such a way that practically no dust escapes. As soon as the cyanamid becomes a part of the mixture the dust is effectively laid by the large excess of other materials, many of which are naturally damp.

GRANULATED CYANAMID

During the past year there was placed on the market in this country a granulated cyanamid, which is practically free from dust. This material is made by pressing damp cyanamid into briquets, which after hardening are ground, and the product screened to sizes between 15- and 60-mesh sieves. On the basis of the original estimated cost of granulating, this improved product was sold at a premium of seven to eight per cent over the price of the powdered material. Actual operation records show, however, that the cost of granulating is more than double this amount. When the price of granulated cyanamid was advanced sufficient to cover the manufacturing expense of producing it, the demand practically ceased. Consumers apparently will not pay a premium of fifteen per cent for dustless material.

AGRICULTURAL USE AND VALUE

Perhaps the most important question that can be asked about cyanamid is: What is its fertilizing value? Does it give to the farmer year after year a consistent profit on his investment, that compares favorably with the profit on an equal expenditure for some other material?

One way to answer the question is to fertilize one-third of a field in the ordinary way with a properly compounded commercial cyanamid mixture, fertilize another one-third with some other standard mixture of equivalent analysis, and omit fertilizers from the remaining one-third. The answer given by such an experiment usually is that cyanamid may be profitably substituted for an equivalent amount of nitrogen in other standard forms.

Unfortunately, a commercial fertilizer mixture is usually regarded by the orthodox scientific investigator as too complex to fit into the logical scheme of his fertilizer test plats. He wants to test the unmixed cyanamid, and he usually wants to use it in quantities far more generous than any that the farmer would ever think of applying. The results of his small plat or pot experiments often do not agree with the farmer's field experience. There are four principal reasons for the difference: (1) Excessive applications of any of the common inorganic ammoniates may cause injury to the plants, and cyanamid is somewhat more active in this respect than the others, (2) cyanamid behaves agricultur-

ally like an organic ammoniate and is not strictly comparable with the other inorganic ammoniates, (3) certain mixtures of two or more different kinds of nitrogen usually give a larger yield than the same quantity of nitrogen in one form alone, and (4) the cyanamid in commercial mixtures is transformed by interaction with phosphates, and loses its identity.

The farmer's use of fertilizers in general is guided solely by the profits derived therefrom. He is continually seeking to learn in what way and in what amounts he shall apply his fertilizers so as to derive a maximum profit. The broad result of this general searching for the best ways is the formation of certain standards of fertilizer practice. These standards are in actual operation on the farms where the most money is being made. For the great staple crops, wheat, oats, corn, hay, and cotton, the application of nitrogen gives increasing profits up to the point where about 200 lbs. of cyanamid or the equivalent thereof in other forms is applied per acre. Above this amount of nitrogen, additional applications will produce additional yields but the value of the extra yield will not, except in the case of very good soils, exceed the extra cost that it took to produce it. Now if cyanamid produces satisfactory results with this maximum economical application, what reasonable objection can there be if it does not produce satisfactory results when used in quantities from two to four times as large? Yet objections have been made against it, based upon such excessive applications in small plat or pot experiments.

The effect of excessive applications of unmixed cyanamid is more evident on acid light sandy soils than on any others. This is probably due to two causes: first, the absorbing power of such soils is low, since the coarse soil particles do not present the large amount of surface that is offered by the much finer particles in the loam and clay soils; and second, bacteria are notably deficient in such soils. The remedies for this situation, if it is necessary to use the unmixed cyanamid, are two: *first*, not more than 250 lbs. of cyanamid per acre should be applied, either spread broadcast and worked well into the soil, or if applied in rows, put down in two applications; *second*, the acid soil conditions should be removed and the bacterial condition improved by the use of sufficient lime, before fertilizing or as a part of the fertilizer. In other words, the object is to avoid too high a concentration of cyanamid in any one portion of soil, and to favor the conversion of the cyanamid to other forms of nitrogen.

Practically, there is no more necessity for applying excessive quantities of one kind of ammoniate, than there is for feeding an animal an excessive amount of one kind of food. There are stock-foods, green clover, for instance, that may kill an animal if fed to excess at one time, and there are many articles of human food that will cause serious illness if eaten to excess, but that is no objection to their use in normal economical quantities. When it is necessary to apply large quantities of nitrogen to certain crops, such as truck crops, potatoes, fancy tobacco, etc., it is customary and desirable to derive the nitrogen from several sources, and not from one only. The use of 200 lbs. of cyanamid per acre in rows, or 300 lbs. broadcast would be economical and satisfactory on such crops, but additional nitrogen should be derived from other sources.

Experience has taught the practical fertilizer manufacturer that a mixture of different forms of nitrogen, properly chosen, almost invariably gives better results than an equivalent amount of nitrogen in a single form. It is well known that different ammoniates yield their nitrogen to the plant in an available form at much different rates, depending upon the nature of the fertilizer, soil conditions, climate, etc. Thus, with respect to the rapidity with which they yield available nitrogen the common ammoniates may be arranged in about the following order, beginning with the most rapid:

1—Sodium Nitrate.
2—Ammonium Sulfate.
3—Cyanamid, Cottonseed
    Meal, Castor Pomace.
4—Dried Blood, Dried Fish,
    Tankage.
5—Steamed Bone, Ground Raw
    Bone.

When applied at the usual rate the quick-acting ammoniates supply an abundance of nitrogen in the early stages of growth, but little or none in the last stages. The slow-acting ammoniates do not supply an adequate amount of nitrogen in the early stages, while those of medium activity are ineffective both in the beginning and in the final stages of growth. It is obvious that a mixture of ammoniates that will furnish a uniform stream of available nitrogen from the beginning of growth to maturity will produce better results than a single ammoniate of equal nitrogen content that furnishes an over-supply of available nitrogen at one time and is deficient at other times.

The above applies only to the economical fertilizing of plants, where just enough nitrogen is added to supply the plants' requirements. Where there is a great excess of nitrogen applied, there is almost certain to be a sufficient supply to meet the plants' requirements at all stages of growth. Even the most active form of nitrogen would last longer than the period of growth of the plant if enough were applied at the start, but such applications would not be economical on account of unavoidable losses.

The common practice, therefore, of estimating the relative value of different ammoniates by measuring their results when applied to a common task is not strictly accurate. Fertilizer materials have as much individuality and are as different in their functions as are different kinds of building material, or different breeds of horses, or different kinds of clothing. Some excel in one respect, and others in another respect. Cyanamid, for instance, may take the place of the organic ammoniates of intermediate activity, because the nitrogen in these materials becomes available at about the same rate, and under the same conditions as cyanamid nitrogen. It cannot, however, act as successfully as sodium nitrate, when the object is to produce forced growth, because cyanamid is not in the class of forcing ammoniates. The fact that a draft horse cannot travel a mile in three minutes argues very little as to his ability as a draft horse.

The great majority of the reports on the fertilizing value of cyanamid as found in the literature, therefore, have little significance for the American manufacturer of fertilizers. The question to which he wants an answer has been very little touched upon. This is: "What is the effect of putting cyanamid in place of one or more of the other ammoniates, especially the expensive organic ammoniates, in fertilizer mixtures?" From observation of practical mixtures, however, the answer is, that cyanamid is a successful substitute for the medium to slow-acting organic ammoniates.

Another reason why results with the pure cyanamid may not hold for the actual cyanamid mixtures sold in America is found in the fact that practically all the cyanamid used in this country is sold to fertilizer manufacturers, and practically all of it is used in acid phosphate mixtures. A very little is used in basic slag mixtures, and a small amount in other ways.

When cyanamid is mixed with acid phosphate there is an immediate reaction, resulting in the complete breaking down of the calcium cyanamid. The calcium is fixed as mono- and di-calcium phosphates—the nitrogen is hydrolyzed to urea. Urea, from the fertilizer standpoint, seems to be the ideal form of organic nitrogen. It is extremely soluble, can be directly assimilated by plants, but if not immediately absorbed, reacts with the soil particles, and becomes fixed as rather insoluble double ammonium salts, that do not easily wash out of the soil. By this chemical reaction therefore, the identity of the original cyanamid is destroyed, and a new set of properties is established, namely, the properties of a mixture of urea nitrogen with mono-

and di-calcium phosphates. This is what the American farmer gets when he buys a commercial cyanamid mixture made with acid phosphate as the source of phosphoric acid. The practical results from such mixtures are, as one would expect, entirely satisfactory.

Basic slag mixtures are used to some extent in the states along the Atlantic Coast. On acid sandy soils basic slag is probably somewhat more effective than acid phosphate, probably owing, in a large measure, to the action of the lime in neutralizing soil acids, and permitting the restoration of bacteria in proper numbers. Slag contains from 15 to 18 per cent iron, and about 5 per cent manganese, both of which are powerful catalyzers of cyanamid to the urea form. The practical experience with these mixtures seems to be entirely satisfactory.

We see, therefore, that practically there is no need of applying more than 200 lbs. of unmixed cyanamid per acre at one time on the staple crops, or 300 lbs. per acre on truck crops. If more nitrogen than this is needed, it should be derived from additional sources. The great majority of the reports found in the literature on cyanamid are practically worthless because the experiments were made with excessive quantities. The only thoroughly satisfactory and valuable test from the farmer's point of view, is one that conforms to the economic requirements that govern the use of any fertilizer, and is made under practical farm conditions. Since practically all the cyanamid sold in this country reaches the farmer as a mixture of urea nitrogen and mono- and di-calcium phosphates, it is only necessary to know what results are being obtained with such mixtures. The reports are almost unanimously favorable.

MIXING WITH ACID PHOSPHATE

The statement can be found in many places in the literature that "Cyanamid must not be mixed with acid phosphate, since thereby the available phosphoric acid is converted to the insoluble form." On charts showing incompatible mixtures of fertilizer materials, the mixtures of cyanamid and acid phosphate are always indicated as not practical. Nevertheless, as was said above, practically all of the cyanamid sold in this country is used in mixtures containing acid phosphate.

In the average phosphate most of the phosphoric acid is in the water-soluble condition (as free phosphoric acid and mono-calcium phosphate), a small amount is present as di-calcium phosphate, not soluble in water but soluble in ammonium citrate solution, and a small amount is present as phosphates insoluble in ammonium citrate solution. When a small amount of cyanamid or other active lime compound is added to acid phosphate, there is an immediate reaction between the lime and the water-soluble phosphoric acid, resulting in a change of the latter to the citrate-soluble form. Both of these forms have about the same agricultural value, and both have the same commercial value. When a large amount of cyanamid is added to acid phosphate, however, there is a more complete neutralization, resulting in the formation of forms containing more lime than di-calcium phosphate contains, and these forms are not soluble in citrate solution; hence, they have no commercial value.

Now it happens that the experiments reported in the literature were mostly made with large quantities of cyanamid, hence the results were unfavorable to such mixtures. On closer investigation of this problem, however, paying attention to the quantitative factors involved, it was found that as the quantity of cyanamid used with respect to the acid phosphate decreased, the loss of available phosphoric acid decreased. When the quantity of cyanamid is as small as 60 to 80 lbs. of cyanamid to a ton of average complete mixture containing approximately 1000 lbs. of acid phosphate, the loss of available phosphoric acid is not appreciable. *It is at this rate that most of the cyanamid sold in this country is used in commercial fertilizers.* In some cases as much as 150 lbs. is successfully used. The acid phosphate must be dry in this case, and as much bulky organic matter as possible used.

MIXTURES WITH AMMONIUM SULFATE

It has also been said that cyanamid must not by any means be mixed with ammonium sulfate, since the lime in the former will drive out free ammonia from the ammonium sulfate. This is true if we consider a simple mixture of only the two substances. It is also true for mixtures of cyanamid, ammonium sulfate and acid phosphate, if large quantities of cyanamid are used. If, however, we pay attention to the quantitative factors again, we find that when there are not more than 150 lbs. of cyanamid present along with ammonium sulfate and 1000 lbs. of acid phosphate, there will be no escape of ammonia from the mixture. The ammonia set free by the lime is caught by the acid phosphate, and fixed as ammonium phosphates. Since the use of acid phosphate with cyanamid imposes a limit of less than 150 lbs. of cyanamid per ton of mixture it is not possible to reach a large enough quantity of cyanamid in such mixtures to cause a loss of ammonia. Hence, in all commercial acid phosphate mixtures, made with due regard to the necessity of keeping the phosphoric acid available, there is no possibility of liberation of free ammonia.

SPECIAL ADVANTAGES

It may not be amiss here to name the special advantages that commend the use of cyanamid to the fertilizer manufacturer: (1) It is a low-priced material; (2) It has a powerful drying-out action on damp materials used in mixtures; (3) It removes free acids from the acid phosphate, thus preventing rotting of bags, and loss of nitric acid from sodium nitrate in the mixture; (4) It adds agriculturally available lime to the mixture; and, (5) It can successfully replace part or all of the more expensive organic materials in a fertilizer.

SUMMARY

I—The cost of food products in the United States has increased about twice as fast as the cost of other commodities, and about twice as fast as the general cost of living throughout the world. This tendency can be offset by an increased crop production, which will lower the price of food products, and hence the cost of living. Fertilizers are the most important single factor in increasing the crop production.

II—Nitrogen is the most expensive and agriculturally most necessary element in commercial fertilizers. A general reduction in the cost of the latter must come through increased production of nitrogen at lower cost. The cyanamid process is probably the cheapest known source of fertilizer nitrogen.

III—The rapid successful development of the economically important cyanamid industry has been full of difficulties, practically all of which have been overcome or minimized by paying attention to the quantitative factors involved.

IV—The greatest common error in the experimental testing of cyanamid has been in the use of excessive quantities. When used in normal agricultural quantities, the results are entirely satisfactory.

V—All difficulties from the farmer's standpoint are removed by the complete reaction of the cyanamid with acid phosphate in commercial mixtures. Such mixtures consume practically all of the American output of cyanamid.

VI—Cyanamid has several special advantages as an ingredient in mixed fertilizers.

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INDUSTRIAL MALTOSE

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It is common knowledge that literature records numerous instances of checks or lapses in the development of various industries or arts. In the field of starch products, the maltose industry is an example of this sort. Its existence has become so obscure, as to have practically disappeared from the public eye.

An examination into this decadence, and as to whether or not it has been a simple case resulting from a survival of the fittest, seems very timely, especially because of its direct bearing on the justifiability of glucose, which, as a product and as a commercial term, is still in active controversy. Sufficient references will be found appended to supply an introduction to the existing literature.

With the possible exception of Japan, where malt-converted or maltose products have been highly esteemed since remote antiquity, cane sugar has generally served as the standard of artificial sweetening, from a very early time. About the beginning of the nineteenth century, owing to the high cost of the established industrial sugar and the persistence of the sweetening habit, attention became effectively awakened with regard to possible substitutes.

This condition became greatly intensified in Europe. About the year 1809, France felt the vital need of some new commercial product that would more or less replace or "piece out" cane sugar. This particular situation was a result from the bearing of the Empire's prolonged conflicts with England upon its supply of Colonial sugar. Ingenuity and invention were stimulated by means of national premiums offered for cane sugar substitutes, and the grape was very hopefully regarded as a source from which an easy and abundant supply of "saccharine matter" could be had. In fact, the first prizes were directed toward competition in respect to syrups and sugar from grapes. A little later, as this source was found to be impracticable, special inducements were extended to cover any one who might discover "the easiest and cheapest process for making syrups, which shall be most like those from cane." Thus it was a general but more particularly a National necessity which demanded a cheap and easily obtainable substitute for cane sugar. Without a doubt these were the stimulating incentives that led to the discovery of the availability of starch as an economical source of syrups and solids which were more or less sweet.

The acid process for the "saccharification" of starch, or rather of starch pastes, was the first in the field. Credit for this discovery and the consequent facilitation of an industry dealing with the commodity now so long known as glucose, is generally conceded to Kirschhoff, in the year 1811. The principle of action upon which this process depends is a non-selective or general one—that is, as opposed to specificity—and essentially for this reason it was relatively simple to develop its practice to a point where the products were easy and cheap to produce as compared with cane sugar.

When the Continental Blockade was raised, the pressure of necessity for sugar substitutions was very materially reduced. The impetus, however, already given to the glucose industry, sufficed to establish a stronghold for it upon the imagination and life of the people. The idea was especially attractive, because of the great novelty of a ready supply of cheap, sweet products of great apparent prospects. The development of the beet sugar industry likewise exerted a sharp influence in minimizing the popular demand for sucrose substitutes. At this period it should be remembered that the science of carbohydrates and proteins was in its infancy, as was also true of dietetics and physiological chemistry.

It was not until very considerably later that the European maltose industry began to spontaneously develop; that is to say, its inception quite lacked the special features of forced opportunity and the support of an ovation accompanying an apparently unique realization, under which the glucose process was conceived and fostered.

The characteristic sugar of malt-converted products, more difficult to study than the sugar glucose, was not discovered by De Saussure until the year 1819. It remained until 1847 but imperfectly discerned, when Dubrunfaut carried recognition

very much further and gave to this carbohydrate individual the name maltose which it now bears. Although this well defined work upon the part of Dubrunfaut became obscured and the facts were not rediscovered by O'Sullivan until later years, nevertheless, Dubrunfaut himself seems at the time to have had some very clear impressions in regard to the nature and significance of the syrups and sugars which starch was capable of yielding.

However, this may have been, industrially speaking, except with regard to Japan, it is to Dubrunfaut that credit appears to be due as having been the pioneer in the development of malt-converted syrups and sugars. Cuisenier became associated with him, and it was mainly owing to these two workers that the application of the commercially designated maltose products reached the stage attained about the year 1883.

The establishment of glucose had introduced a new factor into a situation theretofore dominated by the products of the cane. The new physical properties of the starch syrup, that had become commercially entrenched, had led to a number of attractive developments in candies, confections, etc., not practicable before. Hence it was that maltose found itself competing in two totally different directions: with glucose against sucrose on the one hand, and on the other by itself against its starch derived predecessor.

Great difficulties were encountered. Although recognition of various merits of the new commodities was readily secured, the processes in use stubbornly resisted every attempt to equalize the manufacturing expense with glucose costs.

ANALYSIS OF PIONEER MALTOSE PROCESSES

The methods that have been and to a limited extent still are employed in the manufacture of industrial maltose may be divided, in a general way, into two classes.

One depended upon the use of very crude starchy materials such as ground maize, corn grits, etc., while the other, by far the less successful, apparently began operations with a more or less impure starch-flour. In either event large proportions of malt were required to effect amylolysis. From fifteen to twenty-five per cent of barley-malt (dry basis) reckoned on the starchy base may be taken as representing that industrial factor.

The general nature of the established processes is well known, and need not be particularized here. Details vary, but all include four essential manufacturing stages, namely, Aqueous Cooking, Saccharification, Refining, and Concentration; and these remain to be dealt with by any specific starch saccharification process yielding edible syrups and solids, except perhaps some future electro-magnetic method which may act effectively upon ungelatinized starch granules, in the presence of neutral or conducting water.

The basic materials were all thick-boiling. By this is meant that constituent starch granules were not modified: they remained in their original state as regards well known paste-forming properties. This was a fundamental impediment. It was not surmounted and from its very nature, as will be shown, its disadvantages could not be overcome.

The chemical and physical properties connotated by the thick-boiling type of the materials operated on, imposed a number of grave peculiarities upon the established processes. Owing to this, aside from the bearing of any other condition, it was mechanically impracticable to reach cooking concentrations which were at all comparable with the densities of first "light liquors" of the glucose industry. Especially was this the case when using more or less impure thick-boiling or unmodified starch itself, freed from the protecting influence of enclosing cellular tissue, thus allowing viscosity effects to fully develop. Such a factor of a greatly depressed limit to initial concentration is fatal to any process wherein low cost of evaporations, and plant and labor minimums, are elements in economic practice.

Low as the mechanical limit was, it could not be utilized be-

cause of the restrictive influence of various chemical and physical properties associated with the thick-boiling character of the crude unmodified bases. Working concentrations, in terms of starch represented in the pastes, as established by cooking operations, needed to be held to a minimum, in order to insure good carbohydrate yields, even though more than liberal use of malt in subsequent treatments was resorted to. Higher initial concentrations lead inevitably and progressively to restriction of diastatic reactivity, and the presence of amylaceous end products or residues of a very slimy and refractory nature. These remainders (the old so-called insoluble starch-cellulose, etc.), in addition to entailing very material direct economic loss, adversely affected filtrations to a hopeless extent.

At this point it should be recalled that in dealing with aqueous starch pastes, in conjunction with characteristic barley-malt amylase (homogenous or composite as it may be) the early stages of amylolysis, comprising extension of simplification, hydration, and solution, are the most difficult for the enzyme to effect. It should also be remembered that restrictive limits or tendencies are encountered depending upon the conditions of existence of the starchy colloids, and more or less hydrated granule residues, that may contribute to the composition of any given paste.

It may be here generally stated, that the controlling conditions involved contain two factors which are to an extent independent and of different significance: one being the qualitative and quantitative extent of hydration of the complex starchy basis of the pastes, and the other the freedom, relative or actual, of the water present, a condition only in part associated with the total water.

Extensive hydration and great freedom of sufficient water are, of course, favorable to enzymic amylolysis, and these desiderata are facilitated by low cooking densities, as is well known.

Thus it was owing mainly to the above outlined circumstances, among them some not obvious or apparent in work conducted at ordinary laboratory concentrations, that in the best practice the use of thick-boiling bases continued to require large proportions of malt and low cooking densities for even adequate completion of solution of the cooked pastes.

Use of large proportions of malt, as demanded by the irrational base, was an incurable disadvantage in itself. It was expensive in first cost. It contributed large percentages of objectionable nitrogenous and some other extractives to the sweet liquors in process, and this contamination alone sufficed to fix a quality of crudeness and carbohydrate inconsistency upon the finished products, despite elaborate and expensive refining. The business, moreover, was encumbered and handicapped in a number of ways, through the necessity of dealing with the excessive malt factor in a manner compatible with the conservation of a general enzymic agent and the recovery of an equivalent of its own associated starch.

Crudeness in the raw starchy materials, in lacking purity for the purpose, was an additional basic obstacle. The superfluous constituents tended to impede operations and promote losses in devious ways. In addition to the fact that they seriously increased the difficulty and cost of refining, in the end various contaminating effects could not be eliminated from the finished products. The large percentages and easily decomposable character of the major impurities present contraindicated any advantages that might have been apparent through acidic cooking, as a means of starch liquefaction in the manufacture of high-grade maltose products of great purity, for reasons that may be readily understood, though such considerations may very limitedly apply in alcohol and other manufacture.

It follows then that the practice of ordinary aqueous cooking, commonly under steam pressure, was a limit largely imposed by the impurity of the raw materials. It was, however, a defect of primary magnitude, owing to its leaving the starch paste and granule débris in such physical and chemical shape that

work of great difficulty still remained for the malt to do, requiring impractically large percentages of that commodity.

An additional word may not be superfluous as regards the mechanical limits set to cooking as controlling initial concentration. Some exception might seem to exist in the case of comparatively pure starch or starch-flour in the unmodified condition. It might reasonably appear that acidic cooking should be advantageous in that instance, at least, as it might enable the starch equivalent content to be adequately increased by addition of the raw material during cooking, without exceeding mechanical practicability, because a free acidity would tend to maintain a thinning down effect upon the charge. The answer is that irrespective of the accentuation of evils already indicated that would follow from the application of a method of general hydrolysis to the crude impurities still associated with the starch, it is not advantageous to so influence the density of the cooking charge, inasmuch as to avoid incomplete cooking on the one hand, or overcooking on the other, hydrolytic action upon all of the cooking starch should begin and cease at substantially the same time. This requirement may be clearly recognized as imperative in connection with the enzymic manufacture of typical maltose products, as compared with the relatively unimportant influences of abnormal conversions carried out in glucose practice.

To sum up, it may be stated that the pioneer maltose processes, without exception, developed and declined while shackled by some or all of the limiting conditions which may now be outlined as follows:

1. The basic materials were all thick-boiling.
2. They were impure.
3. Cooking treatments were necessarily restricted essentially to disintegrating effects, and ordinary paste formation.
4. Prohibitive proportions of malt were required.
5. Soluble impurities, or rather undesirable organic and inorganic constituents, were introduced and developed during process to a ruinous extent.
6. Evaporations, size of plant for a given output, the labor involved, etc., were all excessive owing to unavoidably low initial concentration.
7. Refining was expensive and incomplete.
8. The products were crude and relatively costly, and hence of limited utility.

PARTIAL FAILURE OF GLUCOSE PROCESSES

As already mentioned the non-specificity of the principle employed in glucose manufacture made it comparatively easy to develop the resulting type of products so that they were cheap. This absence of specificity, however, results in the development of secondary and even more profoundly decomposing actions during the course of transformation of the starch and its associated impurities. Hence it is that notwithstanding the elaborate and disproportionately costly refining methods resorted to, as following easy first steps, advanced decomposition products remain in the finished glucose to a detrimental extent, along with the peculiar contamination contributed by the refining methods themselves. Moreover, the non-self-limiting action of acid hydrolysis as employed, engenders special losses in yield not shared in common with specific methods. These drawbacks, which are in excess of numerous other objections which are held by many to attach to the use of the glucosic type of starch products (whether acid hydrolyzed or not) as common foods, and certain technical defects to be mentioned later, have not been mastered after a century's continuous experience. The nature of the fundamental reasons and the inherent actions involved justify the statement, at this late day, that they are not likely ever to be mastered.

Efforts have been made to found methods and develop saccharine commodities free from the defects of acid saccharification processes and products, which should be independent of barley-malt. The commercial exploitation of maize maltase, so as to enzymically manufacture glucose, is a case in point. None of these procedures have succeeded so well as those utilizing common diastase, nor have any held out the encouragements of that ancient agent in effectiveness, or in general dietetic desirability and type of results.

GENERAL PRINCIPLES BEARING ON RELATIVE ECONOMICS

Apparent simplification in procedure or detail is properly held to be a criterion of industrial advance. This principle, however, is not universal, because a real simplification in a process as a whole and a reduction in costs may be brought about by radical changes which, superficially considered, may seem not to bring the advance within the general rule. Moreover, as regards the manufacture of food products there are other criteria, and inherent standards, which in the last resort are quite extrinsic to adventitious business policies and artificial markets. It seems certain, however, that industrial maltose does not require that exceptions be invoked upon this score. Apart from other considerations, glucose manufacture, at least as it deals with maize, still retains an incubus in the way of secondary steps which are out of all proportion to the results secured, whereas, abolishment of the primary difficulties of pioneer maltose processes will automatically reduce refining to relatively simple and inexpensive means.

Although obvious, it may not be superfluous to point out that in earlier times, ordinary "green starch" (notably from maize) had not become an easy fact of industry, and that by-product economics had not taken on the remarkable importance of the present day. Certain limitations impressed upon the point of view of the older workers have disappeared. At the early time referred to, the idea of profitable carbohydrate yield seemed to be restrictively associated with the factors of extraction and saccharification in a direct attack upon the starch. Preliminary separations, or refinements, were considered to involve unjustifiable economic waste.

It seems important to remark the significance of the fact that this notion was also associated with glucose manufacture, remaining a formidable and unnecessary handicap until a very recent date, and to emphasize the circumstance that despite the late amelioration of this defect, so far as practicable, glucose manufacture remains heavily weighted by the requirement of excessive refining.

COMPARATIVE VALUE OF MALTOSES AND GLUCOSES

The author's activity in the subject being examined has covered a considerable period of time, and includes somewhat extensive experimental and small scale manufacturing work of an original nature, which will be discussed in a later paper. With the exception of the years 1896–7 and 1902, during which the preliminary experimental steps were taken in connection with the firm of Duryea & Co., in New York and in Sioux City, all the practical work referred to has been executed privately in the author's personal laboratories in New York, during 1904–5, and at Cardinal, Ont., during the years 1906–8, both inclusive. It seems ill-advised to omit to publicly record and submit what appear to be the more important results, conclusions, and views attained.

During the year 1896, the author became convinced that physiological or enzymically manufactured starch products of the maltose type were particularly adapted to direct dietetic uses, because of their natural constitutional suitability. The characteristic sugar and true physiological dextrins of such products seemed exceptionally well qualified to withstand bacteria as encountered in the stomach. In addition, they possessed a blandness and non-irritating quality with respect to the stomach lining by no means universally shared by common sugars. Moreover, while readily subject to normal enzymic completion of availability at the assimilative portions of the

alimentary tract, nevertheless they present conditions which require gradual actions; there can be no excessive rate and total of translation and delivery into the field of active metabolism at any point.

It would appear that these ideas, in agreement with much 'recorded at that time (1896), have been confirmed by the great preponderance of subsequent work in physiological chemistry and in dietetics. Enlightened science approves the normal.

About the year 1907, the author discovered that suitable maltose products possessed commanding technical advantages in the difficult and commercially important art of hard candy manufacture. In order of interest, at this juncture it may not be illogical to dwell briefly on this factor, as it may bear upon the future of industrial maltose.

Certain persisting difficulties associated with the manufacture and use of the glucose type of starch products—particularly acid-converted glucose—are tolerably well known. These are real defects, *i. e.*, are inherent in both manufacture and products. The extreme sensitiveness of d-glucose to merest traces of alkalies on the one hand, and the delicacy of sucrose in relation to acidity on the other, place glucose manufacturers in a quandary. The process employed makes it practically impossible to regularly produce products which are neutral from the points of view of both the d-glucose and sucrose, regarded as raw materials for hard candy-making, unless sophisticating substances are added. The familiar sulfurous friend of the glucose industry, colloquially known as "good old dope"—that is, sulfites in one form or another that are so used—thoroughly exemplifies the desperate character of the requirement in question.

While in principle maltoses resemble glucoses in relation to alkalies, as compared with sucrose, nevertheless in practice, according to the author's experience, the greater inherent technical suitability of maltoses for use in hard candy-making tends, in material measure, to protect these particular products from the mutability of typical physiological sugars. Moreover, as perhaps a matter of minor importance, maltose products, during manufacture, are not necessarily subject to heavy contamination by electrolytes—such as sodium chloride, thus in this case also being free from a well known misfortune of modern glucose. This particular defect of glucose results, of course, from neutralization of the hydrolyzing agent employed. In addition to the influence of NaCl on the palatability of saccharine products, it is generally recognized to have an inverting effect upon sucrose, under conditions of candy manufacture.

Aside from consideration of limitations in the manufacture of the ingredients used, hard candies must not only be dry and non-caramelized when made, but they must remain dry—that is, must not become sticky. Assuming everything else to be equal, typical maltose products of suitable type do not need sophistication, and tend to yield permanently dry candies, as contrasted with the divergent properties of glucose. That this is a basic condition is subject to proof by experimental candy manufacture using chemically pure d-glucose and maltose, as the author has done. Pure maltose-sucrose and pure d-glucose-sucrose candies stand customary cooking conditions equally well, and are very white and dry when made. Subjected to a test of artificial moistening, the author has found that such maltose candies dried out perfectly under usual room conditions and did not show any signs of "running." On the other hand the d-glucose candies, submitted to the same tests at the same time, exhibited a strong disposition to dissolve and spread, did not completely dry out, and remained sticky—until finally the free water was taken up by crystallization, quite ruining salable appearance. Glucose products tend towards deliquescence; maltose products exhibit a drying nature. It may be that in the presence of suitable other carbohydrates, and under appropriate conditions, the very strong bond for water which characterizes the sugar maltose may lend itself to thorough non-aqueous saturation by means of carbohydrate compounding.

In brief, numerous practical candy-cooking experiments conducted in the author's laboratories and elsewhere have shown that good industrial maltose products stand cooking heats as well or better than the best glucoses; a given degree of hardness is reached at lower temperatures in the case of maltose; maltose candies present a more attractive appearance in the matter of surface glaze or luster; are blander and more luscious upon the palate—entirely lacking the somewhat acrid after-taste of glucose; and finally, as contrasted with glucose, maltose candies remain dry under all ordinary atmospheric conditions.

It may be correctly said that the chemical individual maltose is not so sweet as d-glucose, which in turn is inferior to sucrose in this respect. Dealing with industrial maltoses and glucoses this seeming deficiency of maltose does not appear. Numerous comparisons on this score between products of approximately corresponding "conversions," for instance, maltoses of $[\alpha]_D = 155°$ and $R = 0.70$ on the one hand, and glucoses showing about $[\alpha]_D = 138°$ and $\kappa = 0.45$ for organic solids on the other, have demonstrated that the sweetness of the momentary first taste may be about the same, but substantially from that point on, in the act of tasting and consuming, the maltoses are indubitably sweeter. As thus compared without flavoring or admixture, high-grade industrial maltose syrups produce a profound impression of superiority upon the palate. The author believes the greater sweetness of the maltoses to be due to the true physiological type of the dextrin components and their ready reaction with salivary ptyalin, thus rapidly developing a large excess of total free sugar, as compared with the glucoses, upon the surfaces controlling the act of taste.

In addition to the factors determining the intrinsic value of the products, touched upon in the foregoing without exhaustion of the list, another and very general consideration remains which cannot be neglected. Whatever the reason or reasons may be, glucoses are universally recognized to be unattractive or unsuitable for use alone; improvement or disguise is a pre-requisite to sale and consumption, even in such a simple and direct application as involved in the case of table syrups. It is certainly a circumstance of extraordinary significance that commercial glucose, after a century of continuous effort and applied experience, should today occupy a surreptitious or submerged position among carbohydrate foodstuffs.

Finally, it is perhaps unnecessary to state that high-grade maltose syrups possess every physical advantage and keeping quality of the best industrial glucoses.

CONCLUSION

The examination embodied in this paper would seem to show that a modern revival of industrial maltose, if practicable, would present many advantages, and furthermore, that such a development is by no means fanciful, provided only that radical and correct solutions be found for pioneer problems. The glucose industry, by nature, does not appear fitted to survive.

The foregoing review and discussion, and the references appended have seemed desirable in order to coördinate the subject in outline in an accessible manner. The presentation is intended further, in avoidance of excessive complexity and length, to serve as an introduction for a paper shortly to follow, which will submit the ways and means of the new industrial maltose process which has resulted from the author's study of this special aspect of an, to him, exceedingly interesting field of industrial chemistry.

The subjoined list of references is sufficient for an introduction to the subject, in view of the excellent bibliographies, etc., contained in several of the volumes noted. For first attention, the author would venture to particularly recommend Effront's

(Prescott) "Enzymes and Their Applications," and Sadtler's "Industrial Organic Chemistry" in so far as it covers "Manufacture of Maltose."

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MILLING OF WHEAT AND TESTING OF FLOUR[1]
By HARRY McCORMACK

There is one great industry which thus far has depended very little on the service of the chemist and chemical engineer in the preparation and marketing of its products. I refer to the wheat and flour milling industry.

During the year 1912, approximately 400,000,000 bushesls of winter wheat valued at $323,000,000 and 330,000,000 bushels of spring wheat valued at $231,000,000 were produced in this country. Practically all of this wheat is marketed as such or made into flour and marketed with no particular reference to its chemical composition. No particular attention is paid to the composition of wheat which is used for seed, as the product obtained from it is sold on optical inspection rather than on chemical analysis.

The principal markets for wheat in this country are: Chicago, Minneapolis, Duluth, St. Louis, Milwaukee, Kansas City and Omaha. The rules of the Boards of Trade governing the inspection and grading of wheat received in these markets are not uniform so that a dealer in Minneapolis selling wheat to Chicago parties may have wheat of one grade in Minneapolis and find that it is wheat of another grade when it reaches Chicago. This fact has accounted for much of the difficulty encountered by grain dealers under inspection of Federal Officials seeking to enforce the Pure Food Laws.

The grading of wheat on the Chicago market may be taken as typical of the grading at all of the principal markets mentioned, as the differences are not very marked and all of them recognize the same varieties and grades of wheat, *viz*:

Winter Wheat, Spring Wheat, Pacific Coast Wheat and Mixed Wheat. The Winter Wheat is classified as: White Winter Wheat, under which there are four grades depending upon the weight per bushel and the percentage of other varieties of wheat present in the mixture; and the same number of grades of Red Winter Wheat and Hard Winter Wheat, depending upon the same conditions. Under the division of Spring Wheat, we have the sub-divisions: Hard Spring Wheat, Northern Spring Wheat of which there are four grades: White Spring Wheat with four grades corresponding to those under Spring Wheat, Durum Wheat of which there are four grades and Velvet Chaff Wheat of which there are four grades. The Pacific Coast Wheat is Red or White; each of these have three grades, depending as do the other wheats on the weight per bushel and the percentage of dirt and mixed varieties present with it.

The grading of this wheat, as it comes on the market, is primarily a matter of the exercise of judgment on the part of the buyer and seller. Many times their decision is at variance with that of the grain inspector or his judgment may conflict with that of either the buyer or the seller. In such a case there is no definite recourse for any of the parties concerned. The question can be decided only by the judgment of parties not interested

in the transaction, but who have no more definite basis for their opinion than have the first parties concerned.

This condition of affairs has led some of the large millers and also some of the large grain companies to seek the services of the chemist, to see if a more satisfactory basis for trading in wheat cannot be reached. The present paper aims to present some of the problems encountered in the attack on this problem and will attempt to point out some of the conditions which it will be necessary to meet before the handling of wheat on a scientific basis is possible.

Grain dealers primarily interested in the establishment of a scientific basis for buying and selling of wheat are those who really buy and sell wheat, not mere traders on the Board of Trade and, in addition to this, they are the dealers whose trade is largely with the milling interests. The miller, of course, is interested primarily in securing a wheat which will give him a satisfactory flour with as large a yield of the better grades of flour as is possible. By the term satisfactory flour, we mean a flour which corresponds in grade to the customary product of his mills and which meets the demands of his customers. It may be a so-called Hard Winter Wheat flour, a Soft Winter Wheat flour, a Hard Spring Wheat or a Soft Spring Wheat. These names are supposed to refer to the wheat from which the flour is milled, but do not always. We have many instances in which Winter Wheat flours contain no Winter Wheat and other instances in which Spring Wheat flours contain no Spring Wheat. At the same time these flours must meet in a general way the prevailing demands for color and texture, which are supposed to be characteristic of flours milled from these varieties of wheat.

A person not familiar with the variations in wheat composition may be of the opinion that wheat of the same variety, from the same locality, will not vary much in composition from season to season. This, however, is incorrect as has been shown by the work of Le Clerc and others who have studied the effect of varying climatic conditions on the same variety of wheat. Further than this it has been shown by the same investigators that the same variety of wheat grown in different localities will change very materially in composition. Taken in connection with this, it is necessary to state that a grain dealer in the largest market rarely has accurate information as to the precise origin of the sample of wheat he is purchasing. These statements indicate the necessity for a constant examination of the samples of wheat being purchased.

We must realize, at once, that the laboratory milling of a wheat cannot be done in the same manner as in the mills of the large flour manufacturers. We must then, at the outset, take into account the fact that it is impossible for us to mill experimentally a flour which can be compared directly to the flour produced in the large mill and at this point, it may be well to say that the grading and testing of flour is very largely a matter of comparison. The miller desires a wheat as has been said, which will give him his customary flour. The wheat which will do this is determined by milling it experimentally and comparing the flour produced with the flour he is producing in his mill. This will mean that if the comparison is to give any indication as to the value of the wheat in producing the desired flour, the methods of milling the wheat must be the same at all times for the same variety of wheat. Any variation in the milling will produce a variation in the flour and thus an incorrect opinion as to the value of the wheat may be deduced. This is shown very clearly in Tables A and A1 which give the results obtained on the same sample of wheat sent to several laboratories, these being the ones best known to the milling trade and with the highest reputation for the character of their work. These tables show, very clearly, that each laboratory has its own method of milling and to some extent its own method of testing a flour obtained by this milling. The majority of laboratories milling wheat and testing flour have approximately the same

laboratory milling equipment, yet the way they conduct the milling differs and leads in most instances to quite different results. Table A shows the comparison of the flours produced, using a soft Winter Patent as standard. Table A1 gives the original data from which these comparisons on Table A were computed.

The milling apparatus employed in preparing the flours, the data upon which are presented in this paper, is a Standard Type of Experimental Milling Equipment and will, therefore, be described at this time.

crease dirt, a considerable portion of the outer bran coat, and the beard from the end of the kernel. The scourer is capable of wide adjustment to suit various sizes of stock, and this particular machine was built to scour as closely as possible and also to deliver *all* the product at the exit openings of the scourer, leaving no residual material to contaminate the succeeding sample. A sufficient quantity of wheat, usually 1200 grams, is weighed out for scouring. The loss in scouring is determined and 1000 grams of this cleaned wheat is weighed out for the milling.

TABLE A—COMPARATIVE FLOUR TEST REPORTS ON THE SAME WHEAT BY DIFFERENT LABORATORIES. TWO SAMPLES OF THE SAME LOT OF KANSAS No. 2 HD FURNISHED TO EACH. ALL FIGURES REFERRED TO SOFT WINTER PATENT AS 100 PER CENT PERFECT

	Armour Grain Co.		Lab. C		Lab. D		Lab. B	
Gluten, per cent.................	9.15	9.15	9.5	9.0	9.36	9.68	9.3	9.4
Ash, per cent....................	0.46	0.47	0.44	0.45	0.483	0.466	0.43	0.43
Absorption, per cent............	56.0	56.0	54.7	53.8	54.2	53.3	57.0	57.0
Color..........................	100.0	100.0	100.0	100.0	94.0	93.0	92.0	92.0
Loaves per barrel...............	102.6	102.6	100.0	99.7	100.0	100.6	100.0	100.0
Size of loaf.....................	106.0	106.6	97.9	101.5	105.2	100.5	100.0	100.0
Quality of loaf..................	102.0	102.0	....	....	100.0	100.0	98.5	98.5
Average value...................	102.7	102.7	....	....	99.7	98.4	97.6	97.6
Ferment period..................	100.0	100.0	....	....	111.0	111.0	101.3	101.8
Quality of gluten...............	103.0	103.0	....	....	115.7	109.8	98.6	98.1
Per cent straight flour milled....	65.0	65.5	74.5	75.0	66.49	61.02	67.0	67.5

It will be noted that each laboratory except D milled on the two samples approximately the same amount of flour. The results obtained in testing the flour are fairly concordant, too, where the same amount of flour is milled. Laboratory D, with considerable variation in milling, also shows considerable variation on the values reported for certain tests.

The milling equipment consists of a special Allis-Chalmers Experimental Mill comprising three sets of six-inch rolls and a jig bolting machine. Two sets of the rolls are corrugated: one set 16 and 12 to the inch and the other 24 and 18 to the inch. These rolls grind dull to sharp and the fast roll runs a little more than twice as fast as the slow one. The smooth rolls have a differential of 7 to 10, that is, the fast roll makes 10 revolutions while the slow one makes 7. Accurate adjustment of the rolls is provided by two large screws on the side of each roll, which allow the rolls to be adjusted so that they are in the same plane,

Any successful milling of a wheat requires the very gradual reduction of the wheat to flour and it is in this gradual reduction that the experimental mill falls short of what may be accomplished with a commercial milling equipment. At the same time, the experimental milling must follow along the same lines as the commercial milling if the flour obtained is to accurately represent the flour-producing value of the wheat.

A somewhat extended line of experiments convinced us that it is necessary to decide for each variety of wheat approximately the quantity of straight flour we desire to produce from it and

TABLE A1—REPORTS ON MILLING AND BAKING TESTS ON THE SAME WHEAT BY DIFFERENT LABORATORIES. EACH SENT TWO SAMPLES OF THE LOT OF KANSAS No. 2 HD

	Armour Grain Co.		Lab. D		Lab. B		Lab. C	
Wheat protein......................	10.9	10.7	10.6	11.0	11.01	11.33	10.9	10.8
Wheat ash.........................	1.90	1.92	1.70	1.60	1.55	1.575	1.73	1.73
Wheat moisture....................	12.5	12.7	11.0	10.3	8.68	9.18	12.2	12.2
MILLING TEST								
Wt. wheat milled, grams............	1000.0	1000.0	2000.0	2000.0	985.0	975.0	800.0	800.0
Passes on rolls......................	3 Coarse / 2 Medium / 7 Smooth		Same		6 Coarse / 9 Smooth	6 Coarse / 10 Smooth	3 Coarse / 12 Smooth	Same
Wt. of bran, grams.................	297.0	283.0	78.0	85.0	250.0	250.0	200.0	200.0
Wt. of shorts, grams...............	53.0	62.0	258.0	258.0	80.0	130.0	65.0	60.0
Wt. of flour, grams................	600.0	622.0	1490.0	1502.0	655.0	595.0	535.0	540.0
Flour protein......................	9.15	9.15	9.5	9.0	9.33	9.57	9.3	9.4
Flour ash.........................	0.46	0.47	0.45	0.44	0.483	0.466	0.43	0.43
Flour moisture....................	12.48	12.18	12.80	12.50	12.25	12.50	13.2	13.3
BAKING TEST								
Absorption........................	56.0	56.0	54.7	53.8	54.2	53.3	57.0	57.0
Time of max. exp., min............	167.0	179.0	316.0	328.0	151.0	150.0	180.0	180.0
No. of rises.......................	2.0	2.0	...	...	4.0	4.0	3.0	3.0
Vol. of loaf, cu. in.................	86.1	84.9	186.0	193.0	90.0	86.0	102.2	102.0
Flour per loaf, grams..............	340.0	340.0	340.0	340.0	340.0	340.0	350.0	350.0
Wt. of loaf, grams.................	490.0	492.0	489.0	487.0	410.0	416.0	515.0	510.0

and by two smaller screws to set them parallel. The rolls are thrown "in" and "out" by means of a lever. A mechanical jig bolting machine completes the equipment of the mill. Frames of standard bolting-cloths are made to fit this jig; and as many as four frames may be inserted at one time.

Before going to the mill the wheat must be clean, as that term is ordinarily understood. This is usually accomplished by the use of some sort of fanning mill, which does not, however, remove much dirt from the crease. In these experiments a Eureka Horizontal Close Scourer was used. It removes the

then mill in such a manner as to produce the very best flour possible from the wheat and of the percentage previously determined. Different varieties of wheat are capable of producing different quantities of first-class straight flour and any attempt to produce more than this percentage of flour from these wheats will at once lower the quality of the flour secured.

Our experimental work convinced us that the Northern Spring wheats gave the best straight flour when milled to produce about 66 per cent of product. Hard Winter wheats produced the best flour when milled to about 63 per cent of straight

flour. Soft Winter wheats should not be milled to produce an excess of about 58 per cent of straight flour. A more intensive milling of any of these wheats leads at once to a marked reduction in color and also to an increase in the percentage of ash, both showing that bran particles are finding their way into the flour. This is most marked on the Soft Winter wheats and the result of a too intense milling of a No. 2 Red Soft Winter Wheat is shown in Table B.

The adjustment of the rolls in the experimental mill will be determined by the size of the wheat kernels being milled. The wheat should pass through the rolls set first so that the wheat kernels will be cracked and this as lightly as possible. They

TABLE B—MILLING TESTS ON SAMPLE OF No. 2 RED WHEAT
Showing the Effect of Too Intense Milling

Milled to........	65.5	58.5	Color..........	94.0	101.0
Gluten..........	9.6	9.5	Average value...	95.3	98.5
Ash.............	0.43	0.37	Qual. of loaf.....	96.5	100.5

should then be brought closer and closer together until they finally run almost touching as the wheat receives its final milling on this set of rolls. After each passage through the rolls, the product goes to the sieves. Our customary arrangement of the sieve is to place at the bottom of the jig a No. 11 flour sieve, on top of this a No. 34 bran sieve and on top of this a No. 16 or No. 18 coarse bran sieve. In the first set of rolls only the product remaining on the upper sieve is remilled. When the milling has been completed on the first set of rolls, which will be accomplished in about three passes, the material remaining on both of the bran sieves is passed to the second set of rolls. About three passes on these will be sufficient. The material from both the first and second bran sieves is then weighed up and discarded from further milling operations. Up to this time, only a very small percentage of flour has been produced and has found its way from the flour sieve to the receptacle provided for it. The material remaining on the flour sieve then passes to the smooth rolls for final milling. In our laboratory, it is customary to pass the material through the smooth rolls eight times, with sieving between each passage and with the space between the smooth rolls being made smaller and smaller. Practically all of the flour is produced in this milling on the smooth rolls. The material remaining on the flour sieve after this milling is weighed up and discarded. The material which has passed through the flour sieve is resifted through a No. 13 flour sieve to remove some of the bran particles and dirt which may have escaped the No. 11 sieve and is weighed to give the percentage of flour produced. The flour produced in this way should be very uniform in texture and color, and should be entirely free from any specks of bran or dirt.

The flour thus produced will compare very favorably with the straight flour produced in any commercial mill. It will, of course, not be equal to the patent flour marketed from a commercial mill, as this patent flour is made by taking the straight flour milled and by subjecting it to a system of air separation and seiving to remove much of the bran particles and some of the germ, which otherwise find their way into the straight flour. The patent flour will vary with different mills and brands all the way from 45 per cent to 90 per cent of the straight flour milled.

The milling description, which has been given, applies to wheats which have recently been harvested and which contain their normal moisture content. In case the wheat has been harvested for some months and has lost a considerable percentage of its normal moisture, it is necessary to add water to the wheat and allow this water to be taken up by the wheat before milling. This process is known as tempering and is for the purpose of softening the bran layers so that they will flatten out in the rolls instead of cutting up.

The methods of milling are stated because they are the ones

we found best and not because we believe it is impossible to improve on them. These methods are suggested for use until better ones are devised and until the various laboratories can agree on a common method of milling.

At present each laboratory is a law unto itself in its methods of milling. They are like us, they know their methods are best and have no use for the methods used in any other place. Many of them seem to think the milling of wheat is a secret process and thus instead of disclosing in their reports the methods of milling employed in producing a flour, the testing of which is covered in report, the report is formulated in such a way as to conceal as much of the process as is possible.

This led us to send out some samples of wheat to certain laboratories, these samples being accompanied by a data sheet such as we desired filled out. Most of the laboratories supplied the data requested, but from some of them we were never able to secure statements covering their methods of operation which were complete enough to enable us to make an intelligent comparison between their methods and results and the methods and results as obtained by ourselves and others. The data we were able to secure is shown on Tables A2 to A5 inclusive.

TABLE A2—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES

No. 2 Spring Wheat	Milling, Baking and Chemical Data			
	Armour Grain Co.	Lab. A	Lab. C	Lab. B
Wheat protein..............	14.3	.....	13.1	13.8
Wheat ash..................	1.87	.....	1.8	1.88
Wheat moisture.............	12.1	.....	11.2	12.2
MILLING TEST				
Wt. wheat milled, grams......	1000.0	.....	2000.0	800.0
Passes on rolls..............	3 Coarse 2 Medium 7 Smooth			3 Coarse 12 Smooth
Wt. of bran, grams...........	297.0	.....	93.0	200.0
Wt. of shorts, grams.........	53.0	.....	298.0	65.0
Wt. of flour, grams..........	632.0	.....	1487.0	535.0
Flour protein...............	12.75	.....	12.6	12.3
Flour ash...................	0.49	.....	0.50	0.45
Flour moisture..............	11.56	.....	12.7	13.2
BAKING TESTS				
Absorption..................	56.0	67.0	56.8	61.0
Time of max. exp., min.......	181.0	125.0	310.0	205.0
No. of rises................	2.0	...	.....	3.0
Vol. of loaf, cu. in..........	88.2	38.0	203.0	109.0
Flour per loaf, grams........	340.0	100.0	340.0	350.0
Wt. of loaf.................	494.0	...	494.0	515.0

It is our opinion that most of the variations shown throughout this data sheet are due to variations in milling, as when we sent out flour samples for comparative tests the results were more concordant.

The determinations made in the chemical analysis of the flour are: ash, moisture, total nitrogen, and on some samples gliadin nitrogen.

These determinations were made in the customary way. It is, therefore, unnecessary to describe them further than the following comments:

Ash can best be determined in an electrically heated muffle furnace, first at a low temperature, then increasing to a full red heat.

Moisture can best be determined using a glass tube to contain the sample: a tube about $1/2 \times 3$ inches is used and placed in the oven horizontally. After drying it must be weighed in a telescopic weighing tube as it is highly hygroscopic.

Some trouble was experienced in the distillation for the nitrogen determination when a certain type of safety bulb tube was used. Some of the alkaline liquor was invariably carried over; it is recommended, therefore, that only the form known as the Hopkins safety bulb tube be used.

These determinations are made use of in the valuation of a flour about as follows: the ash tells us in a rough way about

how much of the bran has found its way into the straight flour milled, as the patent flours have the lowest ash of any on the market. The patent flours made from the different varieties of wheat have somewhat nearly a constant ash and by comparing the ash of our straight flours with those of the patent flours obtained from corresponding varieties of wheat, we have a measure of the value of a wheat which is being tested for its production of patent flour.

The moisture determination is used in calculating all of the

TABLE A3—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES

No. 2 Red Wheat — Milling, Baking and Chemical Data

	Armour Grain Co.	Lab. A	Lab. D	Lab. B
Wheat protein	11.5	.....	11.33	11.30
Wheat ash	1.93	.....	1.55	1.82
Wheat moisture	10.7	.....	8.45	11.8
MILLING TEST				
Wt. wheat milled, grams	1000.0	.....	975.0	800.0
Passes on rolls	3 Coarse 2 Medium 6 Smooth		6 Coarse 10 Smooth	3 Coarse 11 Smooth
Wt. of bran, grams	303.0	.....	290.0	195.0
Wt. of shorts, grams	47.0	.....	80.0	70.0
Wt. of flour, grams	606.0	.....	605.0	535.0
Flour protein	9.58	.....	9.41	9.6
Flour ash	0.47	.....	0.45	0.39
Flour moisture	11.32	.....	12.25	12.65
BAKING TEST				
Absorption	54.5	62.0	51.6	57.0
Time of max. exp., min	174.0	113.0	14.0	150.0
No. of rises	1.0	...	4.0	3.0
Vol. of loaf, cu. in	78.5	34.5	96.0	102.2
Flour per loaf, grams	340.0	100.0	340.0	350.0
Wt. of loaf	492.0	...	415.0	510.0

TABLE A4—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES

No. 2 Spring Wheat — Spring Patent as Standard

	Armour Grain Co.	Lab. A	Lab. C	Lab. B
Gluten, per cent	12.75	...	12.6	12.3
Ash, per cent	0.45	...	0.50	0.45
Absorption, per cent	56.0	67.0	56.8	61.0
Color	100.0	87.0	98.0	98.0
Loaves per bbl	95.0	101.8	101.0	99.4
Size of loaf	100.0	...	100.0	100.0
Quality of loaf	100.0	90.0	....	98.5
Average value	98.7	...	....	97.7
Fermenting period	100.0	...	....	103.6
Quality of gluten	100.0	...	....	96.6
Per cent straight flour milled	65.0	...	74.3	67.0

TABLE A5—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES

No. 2 Red Wheat

	Armour Grain Co.	Lab. A	Lab. D	Lab. B
Gluten, per cent	9.58	...	9.68	9.60
Ash, per cent	0.47	...	0.45	0.39
Absorption, per cent	54.5	62.0	51.6	57.0
Color	102.0	95.0	95.5	94.0
Loaves per barrel	100.0	98.3	99.6	100.0
Size of loaf	99.0	90.7	112.4	100.0
Quality of loaf	101.2	97.0	100.0	99.0
Average value	100.5	95.4	101.6	98.2
Fermenting period	100.0	132.8	111.0	102.7
Quality of gluten	98.5	89.3	109.8	97.4
Per cent straight flour milled	65.0	45.0	62.05	67.0

samples tested to a constant basis of moisture content. It is also used in calculating the quantity of water absorbed by the flour in the preparation of a dough of standard consistency.

The nitrogen determination is on the same basis as the ash determination. It is a comparison between the nitrogen of the straight flour and that of the patent flour prepared from the same varieties of wheat. As the nitrogen on the whole wheat is higher than in either the straight flour or the patent flour

prepared from it, the value of the wheat as a source of patent flour varies inversely as the ratio between nitrogen in straight flour and nitrogen in patent flour.

The determination of gliadin nitrogen is made in order to compute the ratio between total nitrogen and gliadin nitrogen. In general, the higher this ratio the higher is the quantity of the flour. Whole wheat flours have the lowest gliadin number and there is a constantly increasing ratio from the whole wheat up to the patent flour. Some determinations of total nitrogen, gliadin nitrogen and the gliadin numbers are shown in Table C.

The testing of the flour for its bread-producing qualities is carried out in all of the laboratories in about the same way and, as previously stated, there is not much difficulty in getting concordant results from different laboratories working on the same sample of flour.

The determinations made in the baking test are absorption, color, the size of the loaf, the texture of the loaf and fermenting period, and from these determinations are calculated the loaves per barrel, the average value of the flour and the quality of the gluten. The absorption is expressed as the quantity of water necessary to add to a hundred parts of flour to make a dough of standard stiffness. The other figures are comparative using the standard flour as 100 per cent on each of the items mentioned.

There are two general types of dough-handling adapted to the baking of tinned bread. These are generally known as the "sponge" method and the "straight dough" method.

In the sponge method somewhat less than one-half of the flour is mixed with an equal weight of water and all other ingredients. It is then allowed to ferment for $1^1/_2$ to 2 hours, depending on the type of flour, and is then mixed with the remainder of the flour and water to make a dough of the proper consistency. It is then allowed to rise twice and is formed into loaves, placed in the pan in which it is to be baked, and allowed to rise a definite amount. It is then baked. The complete operation takes about $4^1/_2$ hours.

The straight dough method is in general the same as the sponge method with the omission of the sponging stage. In other words

TABLE C—PROTEIN AND GLIADIN DETERMINATIONS WITH CALCULATED GLIADIN NUMBERS

Description of wheat from which flour is made	Protein	Gliadin	Gliadin No.
No. 1 HARD SPRING			
1102	11.2	6.62	59.1
1108	11.3	6.70	59.3
No. 1 VELVET CHAFF			
1103	11.4	6.97	61.1
1109	11.6	6.90	59.5
No. 1 BLUE STEM			
1104	11.8	6.92	58.6
1111	11.9	6.92	58.1
DULUTH No. 1 NORTH			
1105	11.3	6.92	61.2
1107	11.7	6.87	59.7
No. 1 HARD SPRING			
1106	11.6	6.95	60.0
1110	11.8	7.07	60.0
SPRING PAT. (purchased)	10.8	7.40	68.5

the dough is mixed to the proper consistency for baking at the very start of operations instead of after a sponging stage. This naturally subtracts the time of sponging from the operation and enables a far larger number of samples to be handled.

In fact, with the same equipment, it has been found that just double the number of samples can be handled in one 8-hour day if the straight dough method is used instead of the sponge method. The quality of the loaves will be uniformly slightly lower, but the results being comparative with each other, this cannot affect the test.

For the above very potent reasons, the straight dough method is used in our laboratory.

THE BAKING TEST

METHOD—A modification of the baking tests as outlined in *Bulletin* 117 of the Kansas State Agricultural College was used, because several things were thought necessary to bring the test into such form that its results would more closely give the actual commercial value of the flour.

For instance it was found that some flours from the red wheats of the southern states could not be baked satisfactorily by the above original method, whereas they are used to good results in practice. The modification that follows gives very good loaves.

In making baking tests on different flours it is above all desirable that the test should be so conducted that the differences in the results should be caused by the inherent qualities of the flour and not by variations due to the method employed. However, in practice the skilled baker adapts his method to suit the different flours he uses, and he remedies the defects in the flour so some extent by the method of baking he uses. Therefore it has been the writer's aim to conduct these tests in such a way as to get as good bread as possible from the different flours, and if necessary to vary the method of baking in some slight details to be able to do this. That such a method will yield results that more closely approximate the results the flour is going to give in actual use is apparent.

The actual baking and its associated tests were made as follows:

THE STRAIGHT DOUGH TEST—In these tests "dough" means a flour mixture that has been subjected to a short period of fermentation and baked as soon as the dough has risen a standard amount. This amount is fixed by preliminary trial and is uniform in all these tests. The short period of fermentation varies from 1 to 3 hours and is secured by using fresh yeast in large quantities.

Before making the dough we must know the percentage of water that the flour will absorb to be of correct stiffness. This is found by weighing out 30 grams of the flour into a strong teacup and running in distilled water from a burette until the resultant dough is "right." The best test that the dough is "right" is to put it on the bottom of the cup in the form of a round ball and watch it for about 3 minutes. If it gradually settles down until it touches the rim of the circle on the bottom of the cup it is satisfactory. If it stays in the original shape it is too stiff, whereas if it quickly subsides and overlaps the edge of the cup it is too thin. This test will be found to be sensitive in careful hands to within $1/4$ cc. on 30 grams of flour. The water that the flour absorbs is figured in percentage.

Now the dough can be made: 340 grams of flour, 10 grams of sugar, and 5 grams of salt are weighed out. The amount of water as determined by the absorption test, less 50 cc., is also measured out. The flour is placed in the pan in which it is to be baked and placed in the constant temperature oven until it reaches 35° C. As many grams of yeast as are necessary for the whole batch of loaves are weighed out and dissolved in enough cold water to just be able to draw out 50 cc. of the resultant solution for each batch of dough: 10 grams of yeast should in this way get into each batch of dough.

When the flour is warmed to the right temperature it is removed from the oven and two-thirds of it is placed in a dish. The water as measured out is heated to 42° C. and the sugar and salt dissolved in it. Then exactly 50 cc. of the yeast solution are withdrawn in a pipette and added to the sugar and salt solution. The temperature of the resulting mixture should be very close to 35° C. This liquid mixture is then added to the flour. The resultant batter is beaten up with a large spoon or spatula until there are no more lumps, which usually takes about 2 minutes. The remainder of the flour is then added and the dough mixed, first by means of spatulas and then the hands, to a ball of well kneaded consistency. After this operation, which usually takes but two or three minutes, the dough is placed back in its pan, which has been buttered in the meantime, and put back in the rising oven where it is kept at 35° C. The dough is weighed at this time to ascertain the loss during the kneading. This loss is unavoidable, and usually is about 15 grams. It is due mostly to evaporation of moisture and sticking of some dough to the hands.

The dough is now allowed to rise the standard amount and if it is a *very* weak flour from a soft wheat, it is immediately baked, but if the flour has any reasonable strength it is knocked down, rekneaded, and allowed to rise a second time, and at the termination of this rise if the dough of one of the loaves shows signs of collapsing that loaf is then baked, otherwise a third rise is used. Most flours coming from sound wheats will stand three rises; they will even need them. The times of rising are carefully noted, and all loaves are baked exactly 30 minutes at 238° C. About $1/2$ to $3/4$ of an hour after the loaf has been standing in the open air, it is weighed, and this weight is recorded as the weight of the hot loaf. This must, of course, be corrected for the small amount of dough lost in the kneading.

In measuring the volume of the loaf it is put in an oblong box that already contains some turnip seed. Then the box is filled with the seed, gently rapped, and the seed leveled off at the top. The seed is poured out and weighed, and from the weight of seed that the box will contain when there is nothing but seed in it, the volume of the loaf can be obtained, since the volume of the box is known. This method has been found to be accurate to within 5 grams of seed, which correspond to about 2–5 cu. in. in volume.

The volume should be measured approximately one hour after removing the loaf from the oven as it will shrink more and more the longer it stands.

GLUTEN EXPANSION DOUGH TEST

This is for the purpose of testing the quality of the gluten and checking the relative fermentation period of the flour. The procedure is identical with that for the straight dough except that 100 grams of flour are used instead of 340 grams, and the other ingredients in proportionate amounts. At the point where the regular dough would be panned, this dough is placed in the bottom of a well greased glass cylinder which is at a temperature of 35° C. and placed in the rising oven at 35° C.

For the first hour no attention is required, but after that the height of the dough and the time should be recorded every 15 minutes; and later when it is evident that the dough is near its maximum volume, every five minutes. When the dough just begins to fall the volume and time are noted. From the difference in initial and final volumes the relative qualities of the glutens are calculated. Since we start with the same amount of flour, the quality of the gluten itself will be equal to the net rise divided by the per cent gluten in the sample. This figure is then referred to the similar figure of the standard flour on a percentage basis.

Another method of performing this test which seems to yield more definite results uses the gluten itself instead of the dough. For this purpose the gluten is washed out of the flour in the usual way, and then 10 grams of each gluten are placed, wet, in a tin cylinder 1 inch in diameter and placed in the bake oven at 200° C. It will be found that the gluten will expand and after twenty-five minutes will have formed a porous column within the tin. The height of this column will be directly proportional to the quality of the gluten.

In making all these tests, there is selected and tested at the same time a flour, the baking qualities of which are known. The results are compared on a percentage basis and in this way the unknown flour is judged.

We are led from our laboratory experience to make the suggestion that some form of mechanical kneading apparatus which can be kept at constant temperature should be used in all of the kneading operations. If this is not done, there is considerable chance for variation in the results obtained for

fermenting period, texture and size of loaf. We also suggest that the color be determined on the samples of flour rather than on the bread and that this color be determined with an instrument such as the Lovibond tintometer and that it be expressed in the number of standard color used rather than by any percentage system which may be based on the standard flour. At present there seems to be a different method of expressing color in use by each laboratory engaged in flour testing.

We may sum up the results we have been able to obtain in our experimental work on the milling of wheat and testing of flour by saying that we are able to secure results which are satisfactory to us in showing the flour-producing qualities of any wheat. We shall qualify this statement by saying that, at the present time, it is very difficult to express our results in such a way that they will convey an adequate understanding of these results to other parties such as millers or flour jobbers.

The primary object of this paper is to present the need for uniform methods to be employed in the milling and testing operations and a uniform method of expressing the results obtained so that any party receiving a report from any laboratory on any particular wheat or flour, will be able to read this report intelligently and to compare it with any other report which he may receive from this or any other laboratory on the same sample of wheat. It is impossible to interest the millers, or to any considerable extent the grain dealers, in the testing of wheat and flour, until they are able to obtain concordant and satisfactory reports on any sample which they may submit.

The first move in the satisfactory solution of this question must be made by the chemist and the chemical laboratories who are seeking the trade of the grain dealer and the miller. The importance of this work may be inferred to some extent by stating that on single days in the past year one firm of grain dealers disposed of, to millers, more than 200,000 bushels of wheat.

Another factor which enters into the importance of such work is that in many years the wheat crops of certain localities are short, while an abundance of wheat of a different variety may be obtainable from other sections. This is very well illustrated by the conditions of the past year, when the winter wheat crop throughout the country was unusually low. Millers using quantities of Winter Wheat in their milling mixture had to pay a considerable premium above the normal price of wheat to secure varieties of wheat they desired. In some instances this premium amounted to 16 cents per bushel or $160.00 per car. Substitutes for the desired varieties of wheat were consequently in demand and these substitutes also brought a considerable premium in price, ranging from 8 to 16 cents per bushel.

You will note, therefore, that any grain company, which by the service of its chemist may be able to pick up any quantity of these wheats so much desired by the millers will thus make a handsome profit above the expense connected with the operation of a laboratory.

The extension of the wheat and flour testing will undoubtedly be determined by: (1) The ability of the chemists to agree upon a uniform method for conducting the testing and in expressing their results; (2) The ability of the chemists to convince the grain dealer and the miller of the profit which may be derived from a satisfactory knowledge of the wheat being purchased.

ARMOUR INSTITUTE OF TECHNOLOGY LABORATORIES
CHICAGO

CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

FULLER'S EARTH

According to official figures as given in the Oil, Paint and Drug annual report, the value of Fuller's earth produced in the United States in 1912 was $305,522, and Florida was the leading producing State. The principal use of Fuller's earth in this country is in the bleaching, clarifying or filtering of fats, grease and oils. The market for Fuller's earth was quiet, but steady through the year, and prices varied according to quality. Imports of Fuller's earth for the fiscal year with comparisons were:

	Tons	Values
1913	16,866	$145,588
1912	16,175	138,111
1911	15,813	125,899
1910	13,192	118,956
1909	11,489	100,269

FINANCIAL AND LABOR CONDITIONS ON ENGLISH RAILROADS

In an editorial comment on the railway situation, during the past year in England, *Engineering* (London), **97** (1914), 322, publishes the following:

"The past year has, on the whole, been a very prosperous one for the railways, but the gross increases have, to a very large extent, been swallowed in additional charges. The London and North-Western Railway Company, for example, have had a record year: the net receipts amounted to $30,722,786, which is an increase of $4,525,000. Expenses, however, increased by $3,472,600, of which a very large fraction is attributable to increased wages. The Great Western Railway Company's receipts again showed an increase of $5,194,350 on the year. At the same time charged increases by $3,482,300. These figures may be taken as fairly typical. The increased wages cost is, of course, not wholly due to increased rates of pay or shorter hours, but in part to the necessity of employing additional hands to meet the necessities of the exceptional traffic. Such additional labor is necessarily somewhat inefficient, and a feeling of good comradeship also has its effect in inducing the old hands to slack off a little, so as to avoid the risk of "working the new men out of a job." In the case of the London and North-Western Company, for example, of the two and one-half million dollars total increase in the pay bill, only one and one-half million was due to the extra rates of pay. The companies have, of course, to pay, in addition, insurance charges, which in the case of the London and North-Western line were equivalent to nearly 1 per cent on the net receipts. The total wages bill is equivalent to about one-fourth the gross receipts. The 4 per cent increase in rates demanded by the railway companies is claimed to be very far from meeting the increased wages cost.

"The very large amount of capital which must be ventured to provide employment for one railwayman is truly remarkable—averaging about $10,000 per head. This is, of course, out of all proportion greater than in other large industries, and the tendency is for it to increase. In the shipbuilding industry the capital risked per workman amounts to no more than $900, according to an estimate made by Dr. J. Inglis.

"One of the great problems of the day is the arrangement of some reasonable *modus vivendi* with labor. Notices for the termination of the existing agreement as to conciliation boards have been handed in pretty generally. To no small extent the difficulty with labor resides in the circumstance that while the men demand more wages, the capital for necessary extensions and developments can only be obtained if these wages are actually earned. The men, however, in many cases object to the adoption of the only means by which this desideratum can be attained, since every improvement in operating methods devised by the

administration of a railway line, by enabling more work to be done per head, checks temporarily rates of promotion. Hitherto, undoubtedly, there has been somewhat too great a tendency to substitute regulations for explanations, and to adopt generally the attitude of the Roman centurion. Direct access to officers or directors with powers of initiative may do much to make matters work more smoothly, and many of the companies are proceeding on these lines. On the Great Eastern Railway, for example, the company is represented on the Conciliation Board by a special director, and a somewhat similar policy is being pursued by other lines. Much of the trouble experienced in the past has been due to a feeling on the part of the men that the companies were evading the terms of various awards. It will be the business of these special diplomatists to remove such apprehensions before matters come to a crisis."

IMPORTS OF SPERM OIL DURING 1913

According to the Oil, Paint and Drug annual report the importations of sperm oil during 1913 were as follows:

Date	Vessel	Barrels
April 28	Hyanthes	150
May 25	Richard W. Clark	4,150
June 1	Bark Alice Knowles	650
June 29	Brig Daisy	375
July 14	Schr. Ellen A. Swift	450
August 8	Schr. A. W. Nicholson	550
August 9	Bark Chas. W. Morgan	1,200
August 15	Schr. John R. Manta	200
September 4	Bark Gay Head	900
October 25	Schr. E. R. Smith	4,555
November 13	Schr. Richard W. Clark	4,425
November 13	Str. Berlin	1,485
Total		19,090

NOTE—On December 31st, the stocks of unsold sperm oil in New Bedford amounted to 1,100 barrels.

POTASH SHIPMENTS DURING 1914

Consul-General R. P. Skinner, Berlin, Germany, states that the executive authorities of the German Potash Syndicate have resolved to authorize the following deliveries for domestic and foreign consumption during the year 1914 in accordance with the provisions of the potash-syndicate law (the amounts being in metric tons of pure potash, K₂O):

	For domestic consumption	For foreign consumption
	Metric tons	
Carnallite with at least 9 per cent and less than 12 per cent K₂O	7,100	100
Raw salts with 12 to 15 per cent K₂O	339,000	141,100
Fertilizer salts with 20 to 22 per cent K₂O	2,300	48,300
Fertilizer salts with 30 to 32 per cent K₂O	4,000	16,000
Fertilizer salts with 40 to 42 per cent K₂O, including potash fertilizer with 38 per cent K₂O	211,300	67,000
Chloride of potash	69,700	187,500
Sulfate of potash with more than 42 per cent K₂O	1,700	55,000
Sulfate of potash-magnesia	200	15,000
Total	635,300	531,300
Grand total		1,166,600

BY-PRODUCT PRODUCERS IN GERMANY

Several German companies have had in operation for some time by-product producer-gas power plants built according to a system invented by an Englishman, A. H. Lymn. *The Journal of Gas Lighting and Water Supply,* **97** (1914), 715, says:

"A large plant on this principle has been in operation with highly successful results for three years at the works of the Zellstoff-fabrik Waldhof, Mannhein (a Company having a capital of from $15,000,000 to $20,000,000) and another plant on Mr. Lymn's system has been built by his German licensees, Messrs. Ehrhardt and Sehmer, for the Badische Anilin- und Soda-Fabrik of Ludwigshafen-Rhein—probably the largest chemical works in the world. It is interesting for us to be able to add that Mr. Lymn's new and improved system has now been adopted by the German Government for their central power station at Heinitz. This plant is at first being constructed for 3000 K.W., but it is intended to double it later on. It will supply gas to large engines built by Messrs. Ehrhardt and Sehner."

GERMAN FOREIGN TRADE IN IRON

In the year 1913 Germany's foreign trade in iron, like her foreign trade as a whole, showed a considerable increase. *Technik und Wirthschaft,* **7** (1914), 213, gives the following data:

EXPORTS	1912	1913
Iron and iron products	$296,450,000	$334,800,000
Machinery	157,575,000	169,600,000
Totals	$454,025,000	$504,400,000

IMPORTS	1912	1913
Iron and iron products	$27,550,000	$26,025,000
Machinery	19,250,000	20,225,000
Totals	$46,800,000	$46,250,000

In weight, the iron exports, exclusive of machinery, reached the figure of 6,500,000 tons, while the total output of iron in Germany and Luxemburg was 19,100,000 tons (metric). The amount exported was 7.5 per cent more than in 1912, but the value of the exports showed an increase of 13 per cent. The reason for this is that the exportation of the cheaper forms of iron fell off

EXPORTS OF IRON AND IRON PRODUCTS

Year	Metric tons
1911	5,380,000
1912	6,042,000
1913	6,497,000

in 1913, while that of finished products increased 15 to 17 per cent. The proportion of raw iron to the total iron export was 13.2 per cent and shows a condition similar to that in Great Britain, where the proportion of raw iron to the total iron exported sank from 25.7 per cent in 1912 to 22.2 per cent in 1913.

In the following table Germany's iron imports and exports for the last two years are classified in four groups; it will be seen here that the amount of machinery exported is seven times as great as that imported, a great increase over 1900, when the exports were only two and a half times the imports.

	IMPORTS		EXPORTS	
	1912	1913	1912	1913
Raw iron, scrap, etc. (metric tons)	493,000	451,000	1,911,000	1,754,000
Rolling mills' products	118,000	125,000	3,304,000	3,801,000
Machinery	78,000	88,000	537,000	594,000
Other products	63,000	42,000	806,000	943,000

It is noteworthy that the exports to Great Britain, British East Indies, East Asia and South America have more than made up for the falling off of the exports to other European countries; even the small amount exported to the United States was doubled. The following table shows the destinations and amounts of the greater part of the iron exported:

	1910	1912	1913
Great Britain	910,000	1,024,000	1,208,000
Belgium	753,000	798,000	648,000
Netherlands	386,000	555,000	595,000
Brazil and Argentine Republic	395,000	381,000	471,000
Switzerland	262,000	356,000	333,000

NATURAL GAS IN CANADA

Remarkable progress is reported for 1913 by the Canadian Western Natural Gas, Light, Heat and Power Co. According to the *Journal of Gas Lighting and Water Supply*, 97 (1914), 639, the daily consumption amounts to some 26,000,000 cu. ft., which is paid for at the rate of 15 cents per 1000. The distribution has a capacity of 33,000,000 cu. ft. daily, but enlargements are in contemplation, since 500 consumers are being added monthly. The pressure in the borings is over 600 lbs. per sq. in., and this is practically as great as when the well was first started. It may, therefore, be assumed that the supply will last for some years. The total capital of the company at the end of 1913 amounted to more than $9,747,000.

TAR AND BENZOL PRICES

The *Journal of Gas Lighting and Water Supply*, 97 (1914), 640, quotes an article in the *Journal für Gasbeleuchtung*, in which appears a diagram (drawn up by Professor Dr. Ost) showing the remarkable fluctuations in the prices of tar and benzol between the years 1880 and 1905. The price of a ton of tar in 1880 was about 30 marks; in 1883 it had risen to 55; in 1887 it was down to about 16; in 1892 it was up to 40 again; from 1889 to 1905 it was round about 20 marks. The variations in the benzol curve are even more remarkable. Between 1885 and 1886 the price of 100 kg. dropped from 400 marks to 40, owing to the advent of benzol washing in coke-oven practice. In 1890 it again rose to 110 marks; in 1895 it was below 27; and in the next year it shot up to 75 again. From 1899 to 1905 it was fairly steady round about 20 marks. The prices in the London market last week were about 32 marks per ton of tar, and 27 to 28 marks per 100 kg. for benzol.

DOMESTIC LIGHTING FIFTY YEARS AGO

The *Journal of Gas Lighting and Water Supply*, 97 (1914), 516, quotes the following paragraph from *The Builder* for Feb. 20, 1864:

"Of late, in provincial towns, and even in some villages, gaslights have been introduced into the dwellings of the working classes—a practice which adds to the cheerfulness of homes and is not more expensive than candles. In Manchester most new houses, of even the third class, have gas-pipes laid on at the time of building. In London this is not so generally done, even in new houses of this class; and to lay the pipes to old ones, by reopening the pavements, is a seldom recurring art. Of late, however, lamps constructed for the use of paraffin or petroleum and colza oils are coming much into use in the houses of the working classes; and it is stated that in the longest days of winter, when light is needed from between four and five o'clock P. M. till between ten and eleven, and also in the morning, the cost is only about 8d. a week. Common candles would come to about a shilling, while the paraffin gives three or four times the volume of light that could be obtained from candles for that money."

GASES IN IRON AND STEEL

An investigation by W. Herwig, *Stahl und Eisen*, 33, 1721, on the gas contained in blisters formed on steel plates during rolling and annealing is quoted in the *Journal of Gas Lighting and Water Supply*, 97 (1914), 502. This gas consists chiefly of nitrogen. The gases evolved during the solidification of iron immediately after tapping from the blast-furnace include large quantities of hydrogen and carbon monoxide; white iron contains more hydrogen, and hot-blast gray iron more carbon monoxide. By heating in a current of hydrogen, the nitrogen in steel turnings was reduced from 0.022 to 0.006 per cent; and, though it was not increased by heating in a current of nitrogen, yet from a mixture of nitrogen and hydrogen in equal proportions a steel was obtained, in one case with as much as 0.052 per cent of nitrogen. The author considered that similar action takes place in the converter. A steel containing 0.04 per cent of nitrogen, when tested, broke without elongation, but was improved by prolonged annealing.

THE CINEMATOGRAPH IN RESEARCH

In an extremely interesting lecture before the Fränkisch-Oberpfälzischer Section of the Verein deutscher Ingenieure [*Zeitschrift des Ver. deut. Ing.*, 58 (1914), 268], Dr.-Ing. Hanz Goetz outlined the part cinematography had played in scientific and technical research and suggested some of the things that may be expected of it in the future. After an introduction giving statistics, describing apparatus and outlining the history of the invention, the lecture takes up the position of moving picture photography among the means of reproducing phenomena to the census. It differs from other means in that it correlates two of the basic quantities that physics deals with, time and extension in space.

The most obvious way in which the cinematograph may act as an aid to science is in recording rare phenomena such as scenes in the life of seldom seen or difficultly accessible animals, unusual surgical operations, etc.—fields in which considerable success has been attained. Its usefulness only begins here, however. Just as the scale of objects may be varied when they are represented graphically, so the time scale of actions may be changed when they are represented by the cinematograph. By an increase in speed, Professor Pfeffer, of Leipzig, has been able to reproduce in three minutes a ten-day period of growth of a horse-chestnut twig; pictures for this reproduction were taken at five minute intervals. A large field for the study of the growth of both plants and animals is thus opened up. Just as slow motions can be hastened so that it is possible to see the total effect in a truer perspective, so it is possible to retard and analyze quick movements, and the limits are only those of the speed with which the pictures can be taken. With the most refined mechanical devices it is not possible to take more than 250 pictures per second, but by illuminating the moving object with regularly succeeding electric sparks and photographing on a film moving continuously rather than intermittently, it was found possible to increase the number of exposures to 2000 per second. Bull has studied the flight of insects in this manner.

From an engineering point of view the cinematograph has been most useful in studying projectiles and their effect on armor plate. Much higher frequencies had to be used than Bull obtained, and the apparatus employed differed from his in not using a mechanical interrupter; in series with the illuminating spark-gap was a large condenser, and in parallel with it a small one; the large condenser is charged by an induction machine, and when it is discharged the small condenser is alternately charged and discharged across the gap. The period of the alternations can be judged with fair accuracy by the tone. Since an explosion can take place in the five-thousandth part of a second, the speed of nine to fifty thousand exposures per second, obtained by this method, is sufficient to furnish interesting results. Since it is obviously impossible to have the camera near the object photographed, a special arrangement is used.

The cinematograph can also be used for making quantitative measurements of movements. The fall of a body has been studied by photographing on the same film the falling object and the hand of a chronograph, and in the same way the action of a steam hammer has been timed.

In these lines the cinematograph has just begun to be developed, and offers great possibilities in solving problems dealing with time and space in fields as wide apart as engineering and biology, and makes possible the study of motions so slow that it has hitherto been impossible to form conception of their whole meaning, or so fast that it has been almost impossible to form any conception of them at all.

CHEMICAL INDUSTRIES IN JAPAN SINCE 1911

Japan's foreign trade has increased considerably in the last year. Imports in 1912 amounted to $318,000,000, in 1913 to $372,000,000; exports in 1912 amounted to $269,000,000, and in 1913 to $321,000,000. Chemical trade has in general shared in this increase; though the establishment of several factories in Japan, financed chiefly by foreign capital, has greatly cut down the importation of some substances such as formalin and acetic and salicylic acids. On January 1, 1911, there were, in Japan, 470 factories producing chemicals or related products; of these 159 manufactured explosives, 83 oils and waxes, 77 pharmaceutical products, 21 rubber, 13 toilet preparations, 30 soaps, 5 dyes, 49 fertilizers, and 33 were unclassified in the official statistics. Germany and England have furnished the larger part of the imports, but in the last three years American competition has made itself keenly felt.

The *Chemiker-Zeitung*, in which appear the above data, publishes also, 38 (1914), 395, the following table of chemical imports for 1911 and 1912:

	1911	1912
Acids: Boric	$ 49,150	61,000
Citric	15,550	20,000
Acetic	5,400	3,450
Carbolic	69,500	135,000
Salicylic	101,400	53,850
Tartaric	24,150	42,700
Alum	5,650	400
Ammonium carbonate	34,250	45,900
Ammonium chloride	....	45,950
Anilin salts	25,100	71,550
Antifebrin	20,450	19,450
Antipyrine	84,550	86,100
Bismuth nitrate	177,150	83,300
Calcium acetate	....	146,000
Camphor, borneol, etc	41,750	16,350
Cocaine salts	39,750	82,250
Explosives: Dynamite	328,750	380,050
Detonators	71,900	42,650
Other explosives	20,150	50,450
Formalin	112,550	59,550
Gelatin	32,950	37,350
Glycerine	408,100	393,300

	1911	1912
Guaiacol carbonate	....	66,400
Glue	156,450	191,100
Magnesium carbonate	8,750	9,150
Milk sugar	28,450	34,050
Morphine salts	49,550	73,850
Phosphorus, yellow	97,800	132,500
Phosphorus, red	185,350	187,600
Potassium chlorate	620,100	650,100
Potassium bichromate	49,450	125,700
Potassium bromide	8,800	25,650
Preparations, medical, alcoholic	....	46,450
Quinine salts	42,300	47,850
Rhubarb	8,700	10,300
Santonin	31,750	76,450
Senega root	42,450	29,250
Sodium borate	38,500	70,600
Sodium bicarbonate	134,100	135,450
Soda, caustic, raw	630,450	584,200
Soda ash	564,550	694,250
Chemicals, aromatic	....	14,950
Other chemicals	1,689,000	1,633,900
Drugs, etc	131,250	66,800

THE PAPER INDUSTRY IN INDIA

The chief difficulty the paper industry in India has to overcome is lack of raw material, since no wood pulp is to be had in the country. This lack is supplied partly by importation, partly by the use of native grasses, and largely by the use of cotton rags, the supply of which may be judged from the fact that in India over 400,000 tons of cotton goods are used annually. Other raw materials are jute and hemp, and experiments are now being made with bamboo and bagasse, so far without practical results. The *Chemiker-Zeitung*, 38 (1914), 109, gives the following figures for the year 1911: India imported 13,500 tons of raw paper materials worth $530,000, of which 5,500 tons came from Sweden, 5,000 from England and 1,600 from Germany. The paper consumption amounts to 70,000 tons annually with a value of over $6,000,000; of this $2,500,000 worth is of domestic manufacture and $3,500,000 worth or more is imported. In 1911 there were seven paper factories in operation with a combined capital of about $2,000,000.

SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY
FORTY-NINTH MEETING, CINCINNATI, APRIL 6–10, 1914
PROGRAM OF PAPERS
GENERAL MEETING

Addresses of Welcome. Hon. F. S. Spiegel, Mayor of Cincinnati, and President Charles W. Dabney, University of Cincinnati.

Response. Theodore W. Richards, President of the American Chemical Society.

The Chemical Problems of an Active Volcano. (Illustrated.) Arthur L. Day.

The Chemical Fitness of the World for Life. L. J. Henderson.

Flame Reactions. W. D. Bancroft.

Chemical Reactions at Low Pressures. Irving Langmuir.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

Floyd W. Robinson, *Chairman*   Glen F. Mason, *Secretary*

1. Address. Floyd W. Robinson, Chairman.
2. Standards of Food and Drug Chemists. Edward Gudeman.
3. The Determination of Mixed Carbohydrates in Infant Foods. T. M. Rector and E. B. Wettengel.
4. The Determination of Tannin in Tea. H. C. Fuller.
5. A Rapid Method for the Determination of Sodium Chloride in Butter and its Substitutes. T. M. Rector.
6. A Rapid Method for the Determination of Unsaponifiable Matter in Fats and Oils. T. M. Rector.
7. The Determination of Caffein in Coffee and Tea. H. C. Fuller.
8. The Official Method for Determining Crude-Fiber as Applied to Cottonseed Meal. Chas. K. Francis.
9. The Arsenates of Lead. H. V. Tartar and R. H. Robinson.
10. The Changes Produced by the Wrapping of Bread. H. E. Bishop.
11. The Determination of Lecithin-Phosphorus in Macaroni and Farinaceous Articles. H. C. Fuller.
12. On the Composition of Lobster. H. S. Bailey.
13. Tomato Seed Oil. H. S. Bailey.
14. The Digestibility of Corn Consumed by Swine. S. C. Guernsey.
15. Chemical Changes Occurring during the Period of Silage Formation. Ray E. Neidig.
16. Preliminary Notes on the Curing of Cucumber Pickles. H. N. Riley.
17. A Graphic Method of Calculating Dietaries and Rations. D. L. Randall.
18. The Hydrolysis, under Pressure, of Sugar Solutions. W. S. Hubbard and W. L. Mitchell.
19. Notes on the Determination of Total Sulfur. Philip L. Blumenthal.
20. Barium in Various Plants. Nicholas Knight.
21. The Non-Uniformity of Drying Oven Temperatures. Lorin H. Bailey.
22. The Analysis of Alkali Soils. C. N. Catlin.
23. Dates: Comparative Cost of, in Akron, Ohio. Chas. P. Fox.
24. The Composition of Gooseberries with Special Reference to Their Pectin Content. E. H. S. Bailey.

25. **A Rapid Method for Commercial Analysis for Marls and Limestones.** O. B. WINTER.

26. **A Method for the Estimation of Calcium, Strontium, and Magnesium in the Presence of Phosphoric Acid and Iron.** O. B. WINTER.

27. **The Chemistry of the Decomposition of Peat and Muck.** C. S. ROBINSON.

28. **Some Pot Experiments with Mixtures with Peat and Manure in Connection with Various Fertilizers.** C. S. ROBINSON.

BIOLOGICAL CHEMISTRY DIVISION

CARL L. ALSBERG, *Chairman*   I. K. PHELPS, *Secretary*

1. **Coagulation of Albumen by Electrolytes.** WILDER D. BANCROFT.

2. **Colloidal Swelling and Hydrogen Ion Concentration.** L. J. HENDERSON, W. W. PALMER AND L. H. NEWBURGH.

3. **The Functions of Ammonia and Phosphoric Acid in the Regulatory Excretion of Acid.** L. J. HENDERSON AND W. W. PALMER.

4. **Partition of the Nitrogen of Plant, Yeast and Meat Extracts.** F. C. COOK.

5. **Comparison of the Various Methods for the Quantitative Determination of Sugar in Blood.** MAX KAHN.

6. **Clinical Studies of the Russo Test.** MAX KAHN.

7. **Urinary Catalase in Health and Disease.** MAX KAHN AND C. J. BRIM.

8. **On the Presence of Oleic Acid in Gastric Contents of Patients Suffering with Gastric Carcinoma.** MAX KAHN AND J. SUBKIS.

9. **The Lipins of Diseased Human Livers.** J. ROSENBLOOM.

10. **The Potassium Content of Cerebrospinal Fluid in Various Diseases.** J. ROSENBLOOM AND V. L. ANDREWS.

11. **The Nitrogen Distribution in Feces.** A. R. ROSE.

12. **A Standard in the Determination of Ammonia by Nesslerizing with the Dubosc Colorimeter.** A. R. ROSE AND KATHERINE R. COLEMAN.

13. **Nephelometry in the Study of Nucleases.** P. A. KOBER.

14. **A Soluble Polysaccharide in Lower Fungi.** A. W. DOX.

15. **The Chemical Dynamics of Living Protoplasm.** W. J. V. OSTERHOUT.

16. **The Physiological Water Requirement and the Growth of Plants in Glycocoll Solutions.** ALFRED DACHNOWSKI AND A. GORMLEY.

17. **The Estimation of Amino Acids as Such in the Soil.** R. S. POTTER AND R. S. SNYDER.

18. **Methods Adapted for the Determination of Decomposition in Eggs and in Other Protein Food Products.** H. W. HOUGHTON AND F. C. WEBER.

19. **Factors Influencing the Quality of American Sardines.** F. C. WEBER AND H. W. HOUGHTON.

20. **The Composition and Nutritive Value of the Proprietary Infant Foods.** F. C. COOK AND F. C. WEBER.

21. **The Electrical Stimulation of Tissue.** OLIVER E. CLOSSON.

22. **A New Apparatus for Determining Crude Fiber in Foods, Feeding-stuffs, and Feces.** (Demonstration.) A. D. EMMETT.

23. **The Carbon Dioxide Excretion as Modified by Body Weight.** G. O. HIGLEY.

24. **Enzymes of the Central Nervous System.** H. M. ENGLISH AND C. G. MACARTHUR.

25. **Proteins of the Central Nervous System.** H. H. MCGREGOR AND C. G. MACARTHUR.

26. **Specificity in the Action of Drugs on Brain and Heart Phosphatids.** C. G. MACARTHUR AND G. H. CALDWELL.

27. **Reduction Processes in Plant and Soil.** M. X. SULLIVAN.

28. **The Passage of Nucleic Acid from Plant to Medium.** M. X. SULLIVAN.

29. **Chemical Studies upon the Genus Zygadenus.** C. L. ALSBERG.

FERTILIZER CHEMISTRY DIVISION

J. E. BRECKENRIDGE, *Chairman*   F. B. CARPENTER, *Secretary*

1. **Chairman's Address. Chemistry an Important Factor in the Fertilizer Industry.** J. E. BRECKENRIDGE.

2. **The Preparation of Neutral Ammonium Citrate.** ERMON D. EASTMAN AND JOEL H. HILDEBRAND.

3. **A Comparison of Neutral Ammonium Citrate with Sodium Citrate and N/10 Citric Acid.** PAUL RUDNICK, W. B. DERBY AND W. L. LATSHAW.

4. **The Separation of Organic Nitrogen from Mixed Fertilizers.** C. H. JONES.

5. **Separation of Phosphoric Acid from Lime.** F. K. CAMERON.

6. **Separation of Potash from Kelp.** (Lantern). F. K. CAMERON.

Committee Reports

Nitrogen. Progress on the Analysis of Commercial Nitrate of Soda. PAUL RUDNICK, *Chairman*.

Phosphoric Acid. G. FARNHAM, *Chairman*.

Potash. J. E. BRECKENRIDGE, *Chairman*.

Phosphate Rock. F. B. CARPENTER, *Chairman*.

Fertilizer Legislation. F. B. CARPENTER, *Chairman*.

INDIA RUBBER CHEMISTRY SECTION

D. A. CUTLER, *Chairman*   DORRIS WHIPPLE, *Secretary*

1. **The Influence of Temperature in the Physical Testing of Rubber Goods.** T. L. WORMLEY AND J. B. TUTTLE.

2. **Review of Report of Joint Rubber Insulating Committee.** DORRIS WHIPPLE.

The main time of the meeting was taken up with a report of the Analytical Committee and a general discussion.

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

GEO. P. ADAMSON, *Chairman*   S. H. SALISBURY, JR., *Secretary*

1. **New Volumetric Determination of Sulfur in Iron Ores.** L. SELINE.

2. **Pitot Tubes for the Measurement of Gas Velocities.** ANDREW M. FAIRLIE.

3. **A Comparison of Various Modifications of the Kjeldahl and Dumas Methods for the Determination of Nitrogen in Coal and Lignite.** A. C. FIELDNER AND C. A. TAYLOR.

4. **The Mechanism of the Reaction between Phenolic Bodies and Active Methylenes.** L. V. REDMAN, A. J. WEITH AND F. P. BROCK.

5. **Fluorescence of Petroleum Distillates.** (Lantern.) B. T. BROOKS AND R. F. BACON.

6. **The Manufacture of Gasoline from Heavy Petroleum Oils.** (Lantern.) B. T. BROOKS, R. F. BACON AND C. W. CLARK.

7. **Some Economic Phases of the Gasoline Supply.** BENJAMIN T. BROOKS.

8. **Absorption of Caustic Soda by Cellulose.** W. D. BANCROFT.

9. **The Stability of Rosin at Slightly Elevated Temperatures. A Correction.** CHAS. H. HERTY AND H. L. COX.

10. **The Chemists' Club.** (Lantern.) WILLIAM L. DUDLEY.

11. **The Chemist, a Growing Factor in Merchandizing.** A. V H. MORY.

12. **The Method of Analysis of Gasoline.** G. W. GRAY.

13. **The Method of Testing Illuminating Oils.** G. W. GRAY.

14. **Coal Ash in Some Unusual Phases.** S. W. PARR.

15. **A Thermoelectric Method of Determining the Purity of Platinum Ware.** G. K. BURGESS AND P. D. SALE.

16. **A Nevada Oil Shale.** CHAS. BASKERVILLE.

17. **The Metallography of Malleable Iron.** J. CULVER HARTZELL.

18. **The Pyrometer in the Assay Muffle.** F. P. DEWEY.

19. **Note on a Cause of Spontaneous Combustion in Coal Mines.** HORACE G. PORTER.

20. **Graphical Studies of the Ultimate Analyses of Coals.** OLIVER C. RALSTON.

21. **A Graphic Method of Classification of Coals.** OLIVER C. RALSTON.

22. **Osage Orange: Its Value as a Commercial Dyestuff.** F. W. KRESSMANN.

23. **Some Preliminary Experiments on the Hydrolysis of White Spruce with Sugar and Ethyl Alcohol Yields.** (Lantern.) F. W. KRESSMANN.

24. **A Method for the Rapid Quantitative Analysis of Brass and Bronze.** (Pb, Cu, Sn, Sb, Re, Zn.) R. E. LEE, J. P. TRICKEY AND W. H. FEGELY.

25. **A Method for the Rapid Quantitative Analysis of Babbitt Metals.** (Pb, Cu, Sn, Sb.) R. E. LEE, J. P. TRICKEY AND W. H. FEGELY.

26. **The Composition and Testing of Printing Inks.** J. B. TUTTLE AND W. H. SMITH.

27. **The Determination of Carbon in Iron and Steel by the Barium-Carbonate Titration Method.** J. R. CAIN.

28. **Determination of Ammonia in Illuminating Gas.** J. D. EDWARDS.

29. **The Iodine Number of Linseed and Petroleum Oils.** W. H. SMITH AND J. B. TUTTLE.

30. **Chemical Jurisprudence.** LOUIS HOGREFE.

31. **Report of the Committee on Alum Specifications.** WM. M. BOOTH.

32. **Report of the Committee on Platinum.** W. F. HILLEBRAND.

ORGANIC CHEMISTRY DIVISION

F. B. ALLAN, *Chairman*   C. G. DERICK, *Vice-Chairman and Secretary*

1. **The Chemistry of Enzymic Action.** (One hour.) J. U. NEF.

2. **The Constitution of Acetylacetone-Thiourea.** W. J. HALE.

3. **A Contribution to the Study of the Constitution of Hydroxyazo Compounds.** WILLIAM McPHERSON AND GEORGE W. STRATTON.

4. **A General Method for the Preparation of Orthoquinones.** CECIL BOORD AND WILLIAM McPHERSON.

5. **The Oxidation of Propylene Glycol.** WM. LLOYD EVANS, E. J. TITZEMANN AND P. R. COTTRINGER.

6. **A Study of the Mechanism of the Grignard Reaction.** L. THORP AND O. KAMM.

7. **The Structure of the Three Dihydro-β-naphthoic Acids.** C. G. DERICK AND O. KAMM.

8. The Rearrangement of Triarylmethyl Azids. J. K. Senior.

9. The Action of Trioxy-methylene on the Aromatic Hydrocarbons in the Presence of Aluminium Chloride. Geo. B. Frankforter and V. R. Kokatnur.

10. Studies on Organic Periodides. I. Periodides of Methacetin, Phenacetin and Triphenin. W. O. Emery.

11. Periodides of Antipyrin. W. O. Emery and S. Palkin.

12. Molecular Rearrangements of Hydrazines. J. Stieglitz and J. K. Senior.

13. The Phosphates of Destearin. R. R. Renshaw and R. R. Stevens.

14. Electromers and Stereomers with Positive and Negative Hydroxyl. L. W. Jones and L. F. Werner.

15. Halogen Substituted Hydroxamic Acids. L. W. Jones and L. F. Werner.

16. Formyl-β-benzylhydroxylamine. L. W. Jones and M. C. Sneed.

17. The Addition Compounds of Dimethylpyrone with Organic Acids. James Kendall.

18. Errors in the Dumas Method for Determining Nitrogen Due to Occluded Gases in Copper Oxide. C. A. Taylor and A. C. Fieldner.

19. The Isomeric Octacetates of Lactose. C. S. Hudson and J. M. Johnson.

20. Substitution in the Benzene Nucleus and in the Side Chain from the Standpoint of the Electronic Conception of Positive and Negative Valences. H. S. Fry.

21. The Salts of Acridine. L. H. Cone.

22. The Action of Halogen on 4-Nitro-m-Cresol. L. C. Raiford.

23. A Simple Method for the Determination of the Accuracy of the Conductance Data of Organic Electrolytes. C. G. Derick.

24. The Ionization Constant of Pyroracemic Acid. C. G. Derick and St. Elmo Brady.

25. Symposium—The Teaching of Organic Chemistry.

I. Theory of Elementary Organic Chemistry. The Teaching of Elementary Organic Chemistry without the Use of Atomic and Molecular Hypotheses. J. B. Allan. Discussion.

II. Theory of Organic Chemistry for Graduate Students. M. T. Bogert. Discussion. What Shall Be the Character of the Advanced Instruction in Organic Chemistry? R. R. Renshaw. General discussion.

III. Laboratory Teaching of Organic Chemistry. The Teaching of Organic Chemistry in the Laboratory. L. W. Jones. Discussion.

PHARMACEUTICAL CHEMISTRY DIVISION

F. R. Eldred, *Chairman*   A. P. Sy, *Secretary*

1. Methods of Analysis of the Forthcoming Pharmacopoeia. H. W. Wiley.

2. Seasonal Variations in the Iodine Content of the Thyroid Gland. Atherton Seidell and Frederick Fenger.

3. Some Peculiarities of Present Food and Drug Laws. Frank O. Taylor.

4. Notes on the Determination of Antipyrine. George D. Beal and Duane T. Englis.

5. Further Notes on Lloyd's Reagent for Alkaloids. S. Waldbott.

6. Estimation of Phenacetin and Acetanilide in Admixture. W. O. Emery.

7. Estimation of Antipyrin. W. O. Emery and S. Palkin.

8. Estimation of Caffeine and Antipyrin in Admixture. W. O. Emery and S. Palkin.

9. Estimation of Phenacetin and Salol in Admixture. W. O. Emery, C. C. LeFebvre and G. C. Spencer.

10. A Method for the Estimation of Podophyllum Resin. W. M. Jenkins.

11. Commercial Papain and Its Testing. H. M. Adams.

12. Some Observations on the Leach Test for Coumarin. William G. Gaessler.

13. Digitalis Ash. Charles T. P. Fennel.

14. The Estimation of Morphine. H. M. Gordin.

15. The Estimation and Variability of Alcohol in Galenicals. L. F. Kebler.

16. Results of the Examination of Some Medical Agents in the District of Columbia. L. F. Kebler.

17. Extraction of Morphine from Aqueous Solution. H. Buchbinder.

PHYSICAL AND INORGANIC CHEMISTRY DIVISION

G. A. Hulett, *Chairman*   R. C. Wells, *Secretary*

1. Rapid Determination of Arsenic in Poison Cases with the Marsh Test. James R. Withrow.

2. The Decomposition Voltages of Salts in Liquid Ammonia. I. The Ammonium Salts. H. P. Cady and C. A. Nash.

3. Adsorption and Stabilization. J. C. Blucher and E. F. Farnau.

4. The Ideal Diffusion Coefficient and a New Fundamental Law of Diffusion. G. McP. Smith.

5. Further Observations on the Preparation of Selenic Acid and Selenates. Philip L. Blumenthal.

6. Concerning the Atomic Weights of Carbon and Sulfur. T. W. Richards and C. R. Hoover.

7. The Critical Point and the Significance of "b" in the Equation of Van der Waals. Theodore W. Richards.

8. The Present Status of the Absolute Scale of Pressure. Theodore W. Richards.

9. A Method for Producing a Reproducible Contact Potential between Liquids. E. P. Schoch.

10. The Relation between the Concentrations and the Potential of the Ferrous-Ferric Salt Pole. (Lantern.) E. P. Schoch.

11. New Electroanalytical Methods for Lead, Tin, Copper and Antimony. (Lantern.) E. P. Schoch and D. J. Brown.

12. Contribution to the Knowledge of the Actinium Series. Herbert N. McCoy and Edwin D. Leman.

13. Solutions of Some Formates and of Hydrogen Chloride in (Anhydrous) Formic Acid. Cases of Agreement of Strong Electrolytes with the Equilibrium Laws. H. I. Schlesinger and A. W. Martin.

14. Vapor Pressures in Alcoholic Solutions. O. F. Tower.

15. Arsenious Oxide as a Starting Material in Acidimetry. Alan W. C. Menzies and F. N. McCarthy.

16. Equilibria in the Systems: Water, Acetone and Inorganic Salts. Geo. B. Frankforter and Lillian Cohen.

17. The Colorimetric Determination of Manganese by Means of Periodate. H. H. Willard and L. H. Greathouse.

18. Electromotive Behavior of Soluble Sulfides. R. C. Wells.

19. The Phase-Rule Investigation of Addition Reactions. (Lantern.) James Kendall.

20. Peculiar Action of Iodine. Charles T. P. Fennel.

21. Distribution of Caffeine and Antipyrin between Chloroform and Aqueous Solutions. W. O. Emery and C. D. Wright.

22. Reaction in Non-Aqueous Solvents. O. L. Barnebey.

23. Separation of Potassium from Sodium by Extraction of their Chlorplatinates with Acetone. O. L. Barnebey.

24. The Action of Potassium Amide on the Amides of Silver, Barium, Strontium, Calcium, Lithium and Sodium. Edward C. Franklin.

25. The Action of Potassium Amide on Cadmium, Nickel, and Chromium Salts in Liquid Ammonia Solution. Edward C. Franklin.

26. Gas Analysis by Liquefactions and Fractionations. (Lantern.) G. A. Burrell and F. M. Seibert.

27. The Condition of Natural Gas in the Earth's Strata. (Lantern.) G. A. Burrell and F. M. Seibert.

28. Collisional and Diffusional Viscosities. Eugene C. Bingham.

29. The Chemical and Heat Energy of Molecules, Atoms, Sub-Atoms, and Electronic Energy. F. P. Seibel.

30. Electrostenolysis. Harry N. Holmes.

31. A Burette Calibrating Pipette. C. W. Faulk.

32. Preparation of a Standard Magnesium Salt Solution. C. W. Faulk and O. R. Sweeney.

WATER, SEWAGE AND SANITATION SECTION

Edward Bartow, *Chairman*   H. P. Corson, *Secretary*

1. Sanitary Survey of White River. (Illustrated.) John C. Diggs.

2. Hypothetical Combinations in Reporting Water Analyses. R. B. Dole.

3. New Apparatus for the Determination of Hydrogen Sulfide in Water. George B. Frankforter.

4. Sanitary Survey of the Ohio River by the U. S. Public Health Service. W. H. Frost and H. W. Streeter.

5. The Use of Liquid Chlorine in Treating the Water Supply of Indiana Harbor, Ind. H. E. Jordan.

6. Adaptation to Water Analysis of Potassium as Perchlorate. Clarence Scholl.

7. The Preparation of Standards for the Determination of Turbidity of Water. Francis D. West.

8. Report of the Committee on Standard Methods of Water and Sewage Analysis.

9. Chemical Studies of the Pollution of the Ohio River. Earl B. Phelps.

10. Investigation Relating to the Use of Calcium Hypochlorite as a Disinfectant for Water Supplies. W. G. Tice and C. H. Blanchard.

11. Some Further Results of the Hypochlorite Disinfection of the Baltimore City Water Supply: A Comparison of the Reduction of the Different Members of the *B. coli* Group. J. Bosley Thomas and E. A. Sandman.

12. Filtration and Softening of the Cleveland Water Supply. Hippolyte Gruener.

13. The Relation between Aluminium Sulfate and Color in Mechanical Filtration. Frank E. Hale.

EXCURSIONS

The Cincinnati Filtration Plant is the largest Mechanical or Rapid Sand Filter Plant in the world. It is a part of the New Water Works which comprise an Intake Pier, Tunnel under River, River Pumping Station, two large Settling Reservoirs, Filtration Plant, three Coagulation Basins, Clear Water Reservoir, $4^1/_2$ mile Tunnel to Main Station, Main Distribution Pumping Station, several Sub-Pumping stations and many miles of large distribution pipes. The total cost was over 10 million dollars including properties, rights of way, etc.

The purification system, including two settling reservoirs of about 400 million gallons capacity, three coagulation basins of about 22 million gallons capacity, filtration plant and clear water reservoir, cost about $2^1/_2$ million dollars.

The filtration plant consists of a chemical house, head house and filter house. There are 28 filter units with a total capacity of 112 million gallons per day. All valves, over 200 in number, are electrically operated.

The bacteriological and chemical laboratories are used for controlling the operation of the plant. The laboratory force consists of a chief chemist and bacteriologist, one assistant and a helper.

Since the operation of this plant the city has had an uninterrupted supply of pure, clear and sweet water, and typhoid fever has been reduced over 80 per cent.

Over 150 members and guests of the Society visited this plant; this was a large number considering the fact that there was a steady downpour of rain during the entire afternoon.

The Globe Soap Company Plant at St. Bernard consists of seven buildings connected by 2 miles of private railroad track in an area of 23 acres. The entire factory is steam-heated and electrically equipped. About 75,000,000 lbs. of soap products are produced annually requiring approximately 100,000,000 lbs. of raw materials; 100 cars per day can be unloaded and loaded; about 275 persons are employed and the company maintains a Local Secretary who works directly under the Local Y. M. C. A. carrying on welfare and community work.

Five Chemical Engineers are employed and the entire manufacturing process from start to finish is under strict chemical control.

The Proctor and Gamble Plant at Ivorydale occupies 58 permanent and 22 somewhat temporary buildings in 85 acres of ground. Including the soap, glycerine, stearic acid, red oil, refined oils, lard compound and Crisco, the business of last year exceeded $50,000,000.

The power plant is fitted for the most part with Sterling boilers, with automatic stokers, and has a rated capacity of 15,000 H. P. All grades of soap are made as well as of glycerine, including C. P. and that for dynamite manufacture. The soap department equipment includes 64 kettles of 150 tons capacity each.

One main laboratory and several small special laboratories examine all raw materials upon arrival and control products and process. The chemical force includes about twelve chemists in the control and research laboratory, besides a number of chemists who have charge of various departments.

The factory employs a force of 1500. A committee looks after all dangerous places and makes recommendations for alterations or safeguarding employees. For over 25 years a Profit Sharing plan that has proven highly satisfactory to both the company and its employees, has been in operation. There are special provisions for medical attendance and all employees are insured in one of the large Insurance Companies, for which the employee pays a small amount and the company the balance.

A very large delegation visited the Globe Soap Works and the Proctor and Gamble Plant on the afternoon of April 8th leaving the University of Cincinnati in special cars. Dainty souvenirs of products were presented to the visitors and a very refreshing tea was served in the Proctor & Gamble Plant.

The National Cash Register Company Plant at Dayton, covers eight city blocks, has thirty-eight acres of floor space and employed 7600 persons in 1913. The annual payroll is over $6,000,000. The number of registers made in 1912 was 136,489.

RAW MATERIALS USED IN 1912

11,000,000 lbs. sheet steel	183,994 lbs. tin
5,500,000 lbs. foundry metal	135,602 pieces register slabs
6,500,000 lbs. gray iron castings	602,190 locks
6,800,000 ft. of lumber	610,000 yds. textile
5,000,000 lbs. of paper	236,893 pieces glass
3,129,006 lbs. copper	38,392 tons coal

Of the fifteen men on the laboratory staff, there are four chemists, two chemical engineers, two mechanical engineers and two mechanically trained men. Chemical control is accomplished by means of process specifications covering many shop operations such as staining, enameling, varnishing, mixing of alloys, fluxes, etc.

The laboratory controls the operation of the water softener, purity of the water supply, food and milk supply, purchase of materials (80 specifications), fuel and lubrication. As an unusual duty of the laboratory, many talks on simplified physiology and health subjects have been prepared.

The welfare and educational work of this company among its employees is well known to the industrial world.

NATIONAL CASH REGISTER COMPANY ITINERARY

Arrived in Dayton, 9.15 A.M.
Assembled for photograph.
Factory lecture in Hall of Industrial Education. (Illustrated by slides and kinemacolor motion pictures) 9.40 A.M.
Trip through factory (Party divided into groups and furnished with guides), 10.30 A.M.
Luncheon in Officers' Club, 11.45 A.M.
Train for Middletown, 12.45 P.M.

The American Rolling Mills at Middletown, in 1832, made the first crucible steel produced in the U. S. This mill is the home of Ingot Iron. The plant known as the East Works, finished in 1911, is the most up-to-date of its kind in the country.

AMERICAN ROLLING MILLS COMPANY ITINERARY

Address of Welcome, George M. Verity, Pres.
Inspection of East Works, 2.15–3.30 P.M. (Parties divided into groups of twenty-five each; each group in charge of a competent guide).
Route during inspection of East Works: Open Hearth Department; Boiler and Power House; Soaking Pit, Blooming Mill, and Bar Mill; Sheet Mill; Annealing Department; Galvanizing Department; Shipping Department.
Entire party transferred by train to Central Works for inspection of Research Laboratory.
Inspection of Research Laboratory, 3.45 to 4.30 P.M.
Refreshments served in Warehouse.
Train left for Cincinnati, 5.00 P.M.

In his address, Mr. Verity stated that his company are spending large sums on chemical control and research, with the result that many fallacies in methods of procedure have been corrected and their products greatly improved.

The New Cincinnati City Hospital occupies grounds covering 27 acres. The power house is a 2000 H. P. plant, equipped with three dynamos and an ice-making machine, and having four of its boilers equipped for burning natural gas.

The Lloyd Library and Museum contains forty thousand volumes devoted to Botany, Pharmacy, Materia Medica and allied sciences with a section of eclectic medicine. The institution is incorporated, is free to the public, will never be sold, and will always remain a public institution for the benefit of science.

The National Lead Company Plant at Cincinnati is in five acres of grounds, has 75,000 sq. ft. of floor space in its buildings and 60,000 sq. ft. in its corroding yard; 10,000 tons of raw materials are used annually. The employees number 175 and the annual payroll is $175,000. No effort is spared to insure the best working conditions for the employees; locker rooms shower baths, dining and rest rooms and a kitchen are furnished and personal cleanliness required. One chemical engineer supervises the chemical control which is exercised throughout the process.

The Lunkenheimer Company, occupying over 500,000 sq. ft. of floor space, has the largest plant in the world devoted exclusively to the manufacture of high-grade engineering specialties. These include almost numberless articles used in steam and

marine engineering, in motor engines, in automobiles, and allied branches. Much of the company's reputation is based on its valves and fittings for extra high pressure and superheated steam. There are two foundries, one being for the non-ferrous metals and the other for the ferrous metals such as cast-iron, semi-steel, malleable cast-iron and special iron alloys. All departments are under chemical control, for which purpose the plant is excellently equipped with analytical, research and physical laboratories. These laboratories link together the sciences of metallurgy and steam engineering. The fullest provisions are made for preserving the safety and welfare of the employees, and a perfectly furnished hospital is centrally located in the plant and under expert supervision

W. T. Wagner's Sons prepare artificial Mineral and Table Waters from pure distilled water and is one of the two firms in the U. S. that follows the chemical analyses of natural waters as a standard for artificial waters. The factory covers 16,000 sq. ft. of ground with 50,000 sq. ft. of floor space. The factory equipment includes two 100 H. P. Tubular Boilers and a water still having a daily capacity of 2500–3000 gals. All pipe lines and tanks for cold water are of Block Tin and those for steam and hot water lines are tinned copper. Over 600,000 gallons of finished products are made annually. The chief chemist who is a recognized authority on mineral water manufacture is in charge of a very complete research laboratory for bacteriological and chemical investigation, the equipment of which includes a fine Leitz Microscope and Kruess Spectroscope. Proper safety and welfare provisions are provided.

The Eagle White Lead Company uses about 2 million lbs. of raw materials annually and turns out 2¹/₂ million lbs. of finished products. About 250 men are employed on a $200,000 payroll. The plant is under chemical control. The Old Dutch Process of Corrosion is used. In addition to white lead in dry form and ground in oil, other lead pigments are produced as well as Plumbers' Metal Supplies such as lead pipe, traps, bends and solders of Babbitt metals. The welfare work is chiefly done in connection with the habits of cleanliness necessary for good health and safety.

The Wm. S. Merrill Chemical Company manufactures pharmaceutical products and is one of the three oldest concerns in the city. The founder of the business was said to be the first chemist in the Ohio Valley.

The "Icy-Hot" Bottle Company, only five years old, now manufactures 400 models of bottles, jars, carafes, pitchers, luncheon outfits, etc., each embracing the original vacuum principle.

The Fleischmann Company are manufacturers of compressed yeast in the U. S., Canada, Mexico and Cuba. The last ten years have brought about great changes in the methods and processes of manufacture and while originally compressed yeast was a by-product of the distillery it is today the main product of the Fleischmann factories; distilled spirits and distilled vinegar are the by-products of their various plants.

The Frank Tea & Spice Company attribute their success and reputation for pure products to the closest chemical supervision of the products of importation. The firm is one of the largest importers, grinders and manufacturers in this line.

The Dolly Varden Chocolate Company and Colgate & Company expressed their appreciation of what chemical science has done for them by presenting the lady members and guests with souvenirs of their productions.

The Cincinnati Health Department Laboratory exercises the most rigid control of all food products as well as offering free medical attention to all its school children in connection with free clinics.

The National Biscuit Company—Muth's Bakery—makes bread only—over 100,000 loaves daily.

The U. S. Food and Drug Inspection Laboratory is a branch of the Bureau of Chemistry, Department of Agriculture. Its purpose is to carry out the provisions of the Food and Drug Act of June 30, 1906.

The Union Distilling Company Plant was entirely wiped out by fire in 1909 but was rebuilt in 1910 and is now a model as to construction and equipment.

The following plants and institutions were also open to visitors:

Andrews Steel Co.	The Zoological Garden.
Wiedemann Brewing Co.	American Oak and Leather Co.
Old "76" Distilling Co.	J. H. Day Co. (Special Machinery).
James Heekin Spice Co.	Laidlaw-Dunn-Gordon Co. (Pumping Machinery).
American Diamalt Co.	U. S. Public Health Service Laboratory.

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION—REPORT OF COMMITTEE ON ALUM SPECIFICATIONS

[It was voted by the Division that this report be printed in THIS JOURNAL, so as to give time for study and discussion of the specifications included, preparatory to final action at the Montreal meeting.—EDITOR.]

COMMERCIAL ALUM—Shall contain not less than 16 per cent alumina (Al_2O_3) and not more than 1.25 per cent iron (Fe_2O_3).

Shall be free from foreign matter, mechanically mixed through mass.

STANDARD GRADE—Shall be a clean product, containing not less than 17 per cent alumina (Al_2O_3), nor more than 50 per cent iron, figured as Fe_2O_3. Shall be slightly basic.

NEWSPAPER ALUM—1. Must be readily soluble in water.

2. Practically free from insoluble matter other than alumina. (Insoluble alumina in small amount will not be considered objectionable.)

3. It shall contain not more than 1.00 per cent total iron, calculated as ferric oxide (Fe_2O_3), nor more than 0.05 per cent of iron, calculated as ferric oxide and present in the ferric condition.

4. It must contain no free acid.

5. Must contain not less than 17 per cent alumina (Al_2O_3) combined in the form of sulfate and soluble in water.

6. (Optional.) It must, unless otherwise specified, be ground to pass a 10 mesh sieve.

IRON FREE ALUM—1. It must be readily soluble in water.

2. It must be practically free from insoluble matter other than alumina (insoluble alumina in small amount will not be considered objectionable).

3. Must be snow-white in color.

4. Shall not contain more than 0.05 per cent iron, calculated as Fe_2O_3.

5. Must contain no free acid.

6. Shall contain not less than 17 per cent alumina (Al_2O_3) combined in the form of sulfate and soluble in water.

7. (Optional.) It must, unless otherwise specified, be ground to pass a 10 mesh sieve.

FILTER ALUM—1. Must be readily soluble in water.

2. Insoluble matter must not exceed 0.15 per cent.

3. Al_2O_3, at least 17 per cent.

4. Basicity, at least 3 per cent of the total alumina (Al_2O_3) present, i. e., a 17 per cent alum must contain 0.51 per cent basic alumina (Al_2O_3).

5. Iron must be less than 0.65 per cent reckoned as Fe_2O_3.

6. Payment made on actual percentage alumina (Al_2O_3) present.

COLOR MAKERS ALUM—1. Must be readily soluble in water.

2. Insoluble matter shall not exceed 0.15 per cent.

3. Must be free from dark and gritty matter.

4. Al_2O_3, at least 16 per cent.

5. Must be basic.

6. Iron must not exceed 0.01 per cent reckoned as Fe_2O_3.

SAMPLING AND WEIGHING—A separate sample is to be taken

from a number of barrels, in good condition, representing at least 5 per cent of the total shipment, each sample to be taken from the middle of the barrel. The individual samples are to be thoroughly mixed and quartered and reduced down to sufficient size, into two equal portions marked A and B. Each portion is to be immediately enclosed in an air-tight bottle and each bottle marked with initial A or B, with date and car number identifying the shipment.

Portion A is to be considered available for test by purchaser and B is to be considered available for test by seller.

Shipper and consumer are each to sample in this manner at shipping and receiving points, respectively.

In case of disagreement on tests between buyer and seller, all portions of all four samples remaining are to be submitted to independent reference laboratory to be agreed upon, and quality, as determined by said reference laboratory is to be final, and the cost of reference work to be paid by the party most in error.

That portion of a shipment of alum which does not fulfill the requirements upon independent test as herein provided for, as proof thereof may be rejected, the shipper paying the freight both ways on the rejected material; or such shipment may, at the option of the consumer, be accepted and claims made commensurate with the degree of shortage or of inferiority as determined by the herein provided independent investigation.

WM. M. BOOTH.

THE AMERICAN ELECTROCHEMICAL SOCIETY TWENTY-FIFTH GENERAL MEETING NEW YORK CITY, APRIL 16–18, 1914

The Twenty-fifth General Meeting of the American Electrochemical Society was held in New York City, April 16–18, 1914, the sessions being in The Chemists' Club and Earl Hall, Columbia University.

Friday, April 17th was given over to an all-day excursion by steamboat around New York Harbor and Staten Island. The plants of The American Smelting and Refining Company, The United Lead Company and The Waclark Wire Company were visited. This excursion and the Smoker at the Chemists' Club on Friday evening were complimentary to the guests, being tendered by the New York Section of the Society. A Subscription Dinner Dance at The Chemists' Club closed the meeting.

PROGRAM OF PAPERS

Some Economic and Aesthetic Aspects of Electrochemistry. Presidential Address. (Printed in full below.) E. F. ROEBER.

Characteristics of Electrical Energy as Affecting Chemical Industries. C. P. STEINMETZ.

Efficiency of Power Transmission *versus* Utilization in Local Electrochemical Industries. P. SOTHMAN.

Some Economies in the Use of Energy in Electric Furnaces. F. A. J. FITZGERALD.

Power for Electric Furnace Work. W. S. HORRY.

Electrolytic Flames. (Illustrated.) WILDER D. BANCROFT.

Electric Steel Castings. C. A. HANSEN.

Electric Furnaces for Steel Making. EUGENE B. CLARK.

Advantage of Southeastern Alaska for Hydroelectrochemical Industries. W. P. LASS.

Progress in Leaching and Electrolytic Treatment of Copper Ores in South America. E. A. SMITH.

Hydro-electrometallurgy of Copper. ROBERT R. GOODRICH.

Leaching of Copper Tailings. RUDOLPH GAHL.

Metal Inventory in an Electrolytic Copper Refinery. RALPH W. DEACON.

Addition Agents in the Deposition of Zinc from a Solution of Zinc Sulfate. O. P. WATTS AND A. C. SHAPE.

The Effect of Addition Substances in Lead Plating Baths. FRANK C. MATHERS AND O. RALPH OVERMAN.

Electrodeposition of Cadmium. FRANK C. MATHERS AND HUGH M. MARBLE.

Electrodeposition of Nickel. C. W. BENNETT, H. C. KENNY AND R. P. DUGLISS.

Electrolytic Deposition of Brass on a Rotating Cathode. C. W. BENNETT AND A. W. DAVISON.

A New Method for the Determination of Free Cyanide in Electroplating Solutions. GUSTAVE E. F. LUNDELL.

Electric Conduction at High Temperatures and Methods of Measurement. (Illustrated.) E. F. NORTHRUP.

A New Railway Track Cell. E. L. MARSHALL.

Laboratory Notes on Some Electrical Properties of Silver Sulfide. F. A. J. FITZGERALD.

Polarization Single Potentials. CLAUDE N. HITCHCOCK.

New Cell Arrangements for Direct Determination of the Free Energy. REINHARD BEUTNER.

Experiments on White Lead. R. STUART OWENS.

A Microscopic Study of Electrolytic Iron. OLIVER W. STOREY.

The Effect of Addition Agents in the Electrodeposition of Iron. O. P. WATTS AND M. H. LI.

The Permanency of Base-Metal Thermocouples as Affected by their Microstructure. O. L. KOWALKE.

The following papers had already been presented before the New York Section and were discussed:

The Power Problem in the Electrolytic Deposition of Metals. LAWRENCE ADDICKS.

The Power Problem in the Electrolytic Deposition of Metals. H. E. LONGWELL.

Sources of Direct Current for Electrochemical Processes. F. D. NEWBURY.

Improvements in the Metallurgy of Zinc. G. C. STONE.

Electric Zinc Smelting. W. R. INGALLS.

Electrolytic Zinc. JOS. W. RICHARDS.

PRESIDENTIAL ADDRESS

SOME ECONOMIC AND AESTHETIC ASPECTS OF ELECTROCHEMISTRY

By E. F. ROEBER

There is beauty in electrochemistry. The late Ludwig Boltzmann once said that of all artists the mathematical physicist is nearest to the World's creator in the simplicity, directness, and economy of his methods; Boltzmann made this remark in appreciation of the work of Kirchhoff and Maxwell. But we can apply it with equal truth to the electronic theory of our own time which in the simplicity of its fundamental conceptions and in the comprehensiveness of its outlook has all the elements of pure beauty. The intellect which builds the structure of the atoms of the different chemical elements out of a positive electric nucleus in association with varying numbers of negative electrons, and makes his atoms produce the desired result, is a true creator and his model has a beauty like that of the visible world around us.

But more beauty is hidden in electrochemistry than the mathematical beauty of electrochemical theory. The research electrochemist who works out a new process, whether it is the production of aluminum from its oxide or the conversion of amorphous carbon into graphite or the production of calcium carbide from lime and coke or whatever else, proceeds exactly along the same methodical lines as the artist, whether he be sculptor or painter or poet. The artist must take nature as it is. But for his work he takes from nature only what his imagination tells him to be essential to the idea he has in mind. It is this selective copying of the essential from nature and this restriction to the essential that makes a work of art beautiful.

The method is exactly the same with the creative electrochemist. He cannot improve on Nature's processes and methods. All he can do is to imitate or copy Nature's processes and combine them to a certain end. But because his goal is a certain product he can select the starting materials which are essential and use nothing else, and he can select those processes of production which are essential and combine them into the most direct way of production and produce only what is wanted. Artificial graphite made in the laboratory is superior to natural graphite, because nature does not set out to make pure graphite and man does. This makes the economic value of artificial graphite, but it also makes the artificial graphite process in the bold directness of its execution a true work of art. Wherever a process is so designed as to reach its object in the most direct

way with greatest economy, it is beautiful in the eyes of those who understand its rationale and this is broadly true and not restricted to electrochemistry. But the trained engineer's or scientist's intellectual eye is needed to see this type of beauty.

The thoughts on some particular aspects of electrochemistry which I want to submit to you for reflection to-night are of a cognate nature. They refer to the part which electrochemistry plays in the change now going on in modern civilization in economic and aesthetic valuations. Our age is called an age of unrest and revolution. Whether we are really so much more restless than our ancestors is open to discussion and hard to decide. But that the scientific and concomitant engineering advances of the last century have brought an entirely new phase (in the phase-rule sense) into the play of human reactions which make up the history of mankind, is not open to question. That the effects of modern science and engineering go far beyond their spheres of immediate interest is undisputed. What then is the effect of electrochemistry on two apparently so remote fields as political economy and aesthetics?

To express the question concisely I borrow Friedrich Nietzsche's phrase of the revaluation of values. My subject is: How does electrochemistry bring about a revaluation of economics and aesthetic values? I have brought Nietzsche's name into this discussion for still another reason. Nietzsche's brilliant and at first sight extraordinarily daring attempt of a revaluation of ethical values for the sake of creating the "Uebermensch" is perhaps in the final analysis of its positive aspects nothing more than a robust reassertion of what was strong and healthy in the viewpoints and valuations of classic Greece and Rome, but has been lost in the last nineteen centuries to an exaggerated weak sentimentality. Nietzsche wanted to make restitution of this lost strength and health from classic Greece to modern civilization and then create a new ethics. Now, it would seem that the effect of science and engineering on aesthetics is acting at present in the same direction in emphasizing the necessity of a return to the aesthetic viewpoint of classic Greece, as embodied in Socrates' view of the kinship of beauty and utility. It is for this reason that before speaking of aesthetic aspects of electrochemistry it is necessary to take up its economic aspects.

How are economic values being created by industrial electrochemistry? For this discussion Prof. Karl Knies' old and well-known conception is very useful that economic value is of three kinds—*place* value, *time* value, and *form* value. If I may use the text book illustration, ice in winter in the Maine woods has no economic value because there is no market for it there. Brought to New York, it gets place value, because there is a demand for it in New York. Stored and sold in summer time, it gets an additional economic value—time value. Nothing has been done to the ice itself by man. The place value has been created by transportation, the time value by storing, and as we shall see later these two points are of importance for the production of economic values by electrochemistry.

But for the present let us consider the third kind of economic value—form value, *i. e.*, the value created by the work done by man on the materials of nature, comprising mechanical work as well as chemical changes. Any chemical reaction produces or annihilates form values economically speaking. But what is the distinguishing characteristic feature of the form values produced by the electrochemical industries? Let us take a few typical examples.

By the electrolysis of a solution of common salt we get caustic soda and chlorine and we work up the latter perhaps into bleaching powder. The excess of the value of the caustic soda and bleaching powder over that of common salt is the form value produced by this process. So it is in the production of calcium carbide from lime and coke, of nitric acid and nitrates from atmospheric nitrogen and so on.

The fixation of atmospheric nitrogen representing an extreme case is most instructive. The raw material is atmospheric air which as such has no economic value at all, so that we might say that in the production of nitrate from air the economic efficiency becomes infinitely high. It sounds very well to speak of a process with an infinitely high economic efficiency, but if we take the time to remember that exactly this process which is now worked with fair financial results in Norway turned out a commercial failure some ten years ago in Niagara Falls, it is evident that our consideration must have been in some way so one-sided as to be misleading.

Why was fixation of atmospheric nitrogen a failure at Niagara Falls and why is it a success in Norway? Not primarily on account of the process because the Bradley-Lovejoy process worked with about the same technical efficiency as the Birkeland-Eyde process, though the apparatus was considerably more complicated. No, the decisive element which caused failure at Niagara Falls and success in Norway, is the cost of electric power which is three to five times lower in Norway than at Niagara Falls. And this brings us right to the root of the whole matter.

In discussing the economic value of some electrochemical products we have so far in a one-sided way compared only the value of the starting materials and of the end products, but we have entirely neglected the fact that in these cases we have not only to do with materials as such, but rather with the storage of energy in materials. The form value of many products of electrochemical industries is essentially due to their high energy content. A large amount of chemical energy is stored in electrochemical products; it is latent under ordinary condition, but it may be gotten out wherever and whenever necessity arises and this fact makes them useful and economically valuable.

Let us carry this consideration a little further by making use of the conception that the energy of a given system may be considered as the product of two factors—the capacity factor and the intensity factor, to use the terms of Ostwald. The total amount of energy remains the same. But for the engineering applications it makes an enormous difference whether we make the capacity factor small and the intensity factor large or the former large and the latter small.

In case of a waterfall the amount of water passing over the fall in a certain time is the capacity factor, the height of the fall is the intensity factor. The engineering requirements of the development of a waterfall with little water and a high fall are very different from the case of a lot of water with a small fall, though the energy may be exactly the same in both cases.

In the case of electrical energy the current passing in a certain time, measured in coulombs, is the capacity factor, the pressure in volts is the intensity factor. For electric power transmission we make the intensity factor the voltage, as large as possible, in order to decrease the transmission loss.

In the case of electrochemical products, the weight of the materials is the capacity factor, the specific energy stored in them per unit of weight is the intensity factor. If we make the latter high, if we store a lot of energy in a little matter, it will again be favorable as reducing the cost of transportation.

Now the element of transportation brings us to the conception of the place value of electrochemical products. If their form value is due to their high energy content, their place value is due to the possibility of chemical power transmission by material transportation of electrochemical products. These products of the electrochemical industries which are characterized by a high specific energy content are the principal medium of chemical power transmission.

There are two points of chemical power transmission to be specially emphasized. One is that it is not bound to a fixed route. It requires no line wires. It makes use of the ordinary transportation facilities for materials—railways, ships, etc.

This is important as it opens fields for chemical power transmission where electrical power transmission fails. For instance, there are still very large areas in this country, Canada and elsewhere which are so little populated that it would not pay to erect an electric transmission system to provide electric lighting. Here acetylene lighting is of supreme importance. Acetylene lighting is a case of chemical power transmission. At Niagara Falls the electric furnace produces calcium carbide from lime and carbon and chemical energy is thus stored in the carbide which is transported with its energy to any place where acetylene is required for lighting.

If transportation creates place value, storage creates time value. The use of chemical energy after it has been transmitted is not limited to a certain time and that is the second important feature of chemical power transmission. With electrical energy which cannot be stored as such, it is necessary to use the transmitted energy at once or to provide special means for storing it. In this respect chemical power transmission differs essentially from electric power transmission and is superior to it. Chemical energy is in itself essentially stored latent energy and is used, therefore, in connection with other systems of power transmission for storage purposes, as in the case of storage batteries for electric power systems. The time value of calcium carbide is due to the fact that we can store it and can produce the acetylene just at the moment when it is needed for lighting.

There is a long list of electrochemical products which may be considered from the viewpoint of chemical power transmission. In bleaching powder we transmit the possibility of producing a bleaching or a disinfecting liquid whenever and wherever it is needed. In the series of peroxides we transmit their avidity to give off an atom of oxygen when and where we want it, or the reaction caused by it.

As pretty and concrete an illustration of chemical power transmission as we may wish we have in Hans Goldschmidt's ingenious aluminothermic reaction. The heat of reaction of aluminum and oxygen in forming alumina is relatively very high per unit of weight of aluminum. This is just the reason why the economical production of aluminum from alumina did not succeed until electrolysis was resorted to. Now the fundamental idea of the aluminothermic method is that we have in metallic aluminum a medium which gives us by combination with oxygen a large amount of energy wherever or whenever needed. In thermit, the mixture of aluminum and iron oxide, we transport essentially the capability of producing at any place and at any time, highly superheated molten steel for welding rails, for making repairs, and so on.

Again in the new and important Norwegian nitrate industry we have an example of what we may call international chemical power transmission, as the economical value of Norsk saltpeter depends on its easy transportation by ship to other countries. Thus we have at the same time creation of economic values in Norway by building up a new and important industry and creation of economic values in other countries by using Norsk saltpeter to further agriculture.

I have dwelt on the relation of electrochemistry to chemical power transmission at such length because so many electrochemical products can be considered from this viewpoint. But it would be wrong to think that the whole of electrochemistry can thus be viewed. There are quite a number of very important electrochemical products in which with no stretch of imagination I am able to detect time value. But in all cases the form value is high.

In the case of aluminum we have the aspect of chemical power transmission only in the aluminothermic reaction, which though big in itself uses only a small amount of the total output of aluminum. In cooking utensils, in line-wire construction and other applications it is simply the mechanical and electrical properties of aluminum which count and which give it a high form value.

In electrolytic copper refining, the oldest and certainly one of the biggest electrochemical industries, the increase of form value is remarkable. It is a double one: (1) The gold and silver are recovered; (2) the copper itself is considerably increased in form value, due to its greater purity and resulting higher electric conductivity.

All those products of electrochemical industries which have nothing to do with chemical power transmission have a high form value and must have it because otherwise it would not pay to use an electrochemical process in view of the high cost of electrical power. Hence, the well-known axiom that in all such applications the use of electrochemical processes should be restricted as much as possible to the finishing touches, that is, to the refining of a comparatively advanced product.

In addressing the American Electrochemical Society I need hardly show at length how this creation of economic values by the electrochemical industries has affected and is affecting modern civilization in its various phases. What was waste before, and what was considered a nuisance, becomes valuable. When the early Colorado gold seekers discovered the tungsten ores in Boulder Canyon, they cursed them as they were not what they wanted. But "heavy black sand" electrochemistry has given to civilization ferro-tungsten and the tungsten lamp. From culm, the waste material of the anthracite coal mines, Acheson has given to the world artificial graphite with its numerous applications. Then there are the enormous electric-furnace industries of artificial abrasives in use in so many walks of life. And so I could go on through the list of electrochemical products down to Cottrell's electrostatic process of recovering values from obnoxious smelter fumes. I should add, however, that electrolytic copper refining, itself made possible by the dynamo, has paid its debt to electrical engineering and by furnishing firm high-conductivity copper has made modern electric power transmission possible. And as we have seen, in chemical power transmission electrochemistry has brought into modern civilization an absolutely new element by which what is now waste power is being scattered all over the world to build up industries, to further agriculture with fertilizers, to light cities with acetylene, to aid public health with bleaching powder and to affect civilization in general in its most heterogeneous aspects. That electrochemists as true creators are bringing about a revaluation of economic values there can be no doubt. But what has electrochemistry to do with aesthetics?

If beauty is perceived through our senses, the first question is: How has modern engineering affected our senses? The answer is simply that modern engineering has given us artificial senses in addition to our natural senses. In the old days when the apparatus in physical and chemical laboratories were homemade affairs, it was said that experimental physicists and chemists should be able to see with their ears and hear by touch, smell with their tongues and measure temperatures with their eyes. Now modern engineering has given us instruments and apparatus which really represent new senses and which are available to a much more general public. And what is more, our artificial senses can be repaired or replaced by new and better ones and they give us permanent records.

I am not stretching the meaning of the term senses in speaking of instruments as artificial senses. To the electrical engineer the readings of the voltameter and wattmeter are as real and as true indications of the outside world as though he put his head out the window to feel whence the wind blows. Pyrometers give as real, though much more exact indications of temperature, as the touch of a hot body by hand or the trained eye of the furnace man. The photographic camera is a new artificial eye that preserves the record of what it sees. Successive photographs put together in a moving picture show enable us to

crowd into a period of five minutes what may have happened in a year. We can see crystals and plants grow. The electric oscillograph gives us a record that permits us to see in leisure transient phenomena that happen in portions of a second, and study over them for hours. The telephone stretches the ability of the human ear so that it can hear in Denver what is said in New York. And if we hear our children of three or four years talk to us over the long-distance telephone in such a self-evident matter-of-fact way as though they were sitting on our knees, we cannot escape the conclusion that a new generation is rising to which the perception of the outside world comes through new senses and which consequently looks at the world with new eyes. What has electrochemistry to offer to this new generation in aesthetic ideals?

It seems to me that the fundamental contribution which electrochemistry has to make to aesthetics is to carry to its last consequence the principle that waste can never be beautiful. Of course this principle is as old as art. Waste of words in a work of literature, waste of lines or colors in pictures, waste of space in architecture have always been considered the opposite of beautiful. But the growing multiplicity of our sensual knowledge due to the magnified and projected extension of our senses forces us to see waste where our ancestors saw beauty and had a right to see beauty.

Permit me to concentrate my remarks on the one subject that is uppermost in this connection in the minds of American electrochemists—the question of the power development of Niagara Falls. I use it as a clear cut example of what revaluation of aesthetic values by electrochemistry means. The magnificent group of electrochemical industries of Niagara Falls which are the pride of every American electrochemist and should be the pride of the whole American nation suffers seriously from the power famine due to the cessation of power development by international agreement between the United States and Canada. This agreement is based on the alleged will of the people of both countries to have the falls preserved as a scenic spectacle on the principle of conservation of natural beauty. The battle cry is conservation of natural beauty for the people.

The counter-argument has been made that the natural beauty conservationists want to conserve something that no longer exists. With this I agree, but I cannot agree with the expression usually given to this argument, that, if Niagara Falls could be preserved in its original magnificence, it would be worth while but that Niagara as a majestic spectacle has never belonged to the present generation and that its beauty has been given up to noisy and offensive exploitation long before the first power station was created.

This may be true, but it seems to me that this argument does not reach the root of the matter. The beauty of Niagara Falls, like all beauty, is subjective in the onlooker. The question is simply: What do we see when we stand at the brink of Niagara Falls?

Our ancestors who knew nothing of the principle of conservation of energy, of transformation of different forms of energy into each other looked simply at the material side of the Falls and saw beauty and had a right to see beauty. And if we force ourselves into such a one-sided attitude of mind, we can still see beauty.

But if we stand as modern men at the Falls with a free attitude of mind, we don't see simply water, we see power. We see the possibilities of using this power for electric power transmission for lighting, traction, and industrial purposes on a wider area. We see the even greater possibility of storing this power in electrochemical products and utilizing them all over the land in all walks of life. If we look at the Falls with this attitude of mind which is the natural one for us, every cubic foot of water that goes thundering over the falls unutilized appeals to us as waste and nothing but waste.

Now waste can never be beautiful. If the artist's selection of the essential and nothing but the essential makes a work of art beautiful, anything that strikes our imagination as waste must prevent aesthetic enjoyment. If we could look at Niagara Falls with the eyes of our ancestors it would be different, but in full possession of our extended senses which an engineering age has given us, the Falls of Niagara—as much of them as is not utilized—must simply impress us as a waste of immense proportions.

And just the element of bigness which was an element of beauty to our ancestors, has necessarily become to us the reverse, emphasizing only more emphatically the criminal negligence of letting waste on such a tremendous scale go on. Undeveloped, Niagara Falls remains spectacular even to the modern man, but it is no longer beautiful.

The perverse mind of Nero could enjoy the spectacle of Rome burning. A savage tribe could naively enjoy a conflagration that would consume for spectacular purposes a million tons of coal a week. We let the equivalent waste go on in waterpower and hear it called saving beauty for the people.

But there is little use in arguing in aesthetic matters. All we can really do is to make people see for themselves, use their own senses, all of them, their natural ones and their artificial ones. This is what the engineering developments tend to do every day and we can depend upon it that as surely as day follows night, a new generation is rising that will use its senses, all of them, and make its own aesthetics.

When that time has come, the Falls of Niagara running dry will reveal to the world immense beauty, health and wealth scattered by electrical and chemical means all over the country, while the grandeur of the whirlpool rapids, unchanged and undiminished, will have a higher aesthetic value, a deeper meaning of beauty than they can possibly have for us. The world will then smile at the aesthetic scruples of so many well-meaning people of our own time and will wonder what all that talk of saving Nature's beauty was about.

THE AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS—293rd MEETING

The 293rd meeting of the American Institute of Electrical Engineers was held in Pittsburgh, April 9–11, 1914. About 200 members attended.

Wilfred Sykes presided at the first day's session, which was largely devoted to a discussion of the use of electricity in mines. H. O. Swoboda presented a paper on "Self-Contained Portable Electric Lamps," in the course of which he demonstrated an incandescent lamp which may be used in any position and so protected as to resist damage and to prevent the emission of sparks on rough handling.

H. H. Clark discussed "The Regulation of Electrical Installations in Mines." Among other matters dealt with were the rules proposed by the Bureau of Standards, American Mining Congress, and the English and German laws for electrical installations in mines.

The banquet was held on Thursday evening, April 9th. A. M. Dudley, chairman of the Pittsburgh Section of the Institute, delivered the address of welcome.

On April 10th, safe mine operating and the installation of electric signal and telephonic systems were taken up and discussed; and G. M. Eaton read a paper on "The Development of the Electric Mine Locomotive."

On April 11th, the convention closed after trips of inspection to the Westinghouse plants and to the station of the Bureau of Mines.   W. A. HAMOR.

NOTES AND CORRESPONDENCE

THE INVENTION OF CELLULOID

Editor of the Journal of Industrial and Engineering Chemistry:

Being the author of the article on celluloid in the new edition of Thorpe's "Dictionary of Applied Chemistry," from which Prof. Chandler submits a mangled quotation with his emphatic disapproval,[1] and looking back on thirty years' experience in the celluloid industry, I feel constrained to reply to the remarkable statements of the learned Professor.

At the risk of wearying the reader, I must rehearse that part of the history of the nitrocellulose industry which bears on the pyroxylin-camphor compound best known as celluloid. I concede at the outset that the word "celluloid," the registered trade mark, was coined by one of the Hyatt brothers and that several books on the industry, all of them written by outsiders, and some of them not fit for a kindergarten course, ascribe the invention to Hyatt or the Hyatt brothers. Even Beilstein's great handbook falls into this error. All of this goes to show that a legend skilfully launched and brazenly defended is tenacious of life.

The first mention of camphor in conjunction with pyroxylin is contained in the British Patent 1,638 of July 26, 1854, granted to James A. Cutting of Boston, U. S. A., for photographic pictures. Cutting dissolves 32 grains of camphor in a pint of collodion, already containing 80 grains of potassium iodide, and claims by this addition to increase the vigor and distinctiveness of delineation of the positive picture and particularly the half tints, also the beauty of the picture, by giving a fineness of deposit not heretofore attained by any other means. The very nature of his solvent prevented him from observing any solvent action on the pyroxylin due to the presence of camphor, and nobody in his senses will be rash enough to assert that this disclosure of Cutting constitutes the invention of the pyroxylin-camphor compound.

We find the next mention of camphor in the British Patent "MANUFACTURE OF COMPOUNDS OF PYROXYLIN" No. 1313, of May 11, 1865, of Alexander Parkes, Birmingham, the one which the romancers rely on when they try to rob Spill of the credit due him. Parkes mentions in this specification four solvents of low volatility, anilin, nitrobenzol, glacial acetic acid, and camphor, the latter only casually. The three former are specifically enumerated in his claim, but camphor is omitted, a point of significance to any one familiar with patent matters, especially in view of the fact that Parkes and Spill were associates. There is not a word in either this or any other of Parkes' patents that directs the joint use of absolute alcohol and camphor, as has been deduced by some from the famous decision (rendered August 21, 1884) which held Spill's U. S. Patent of November 30, 1869, invalid. In No. 1313 Parkes recommends, as he does elsewhere, absolute wood alcohol or what he conceives to be such; and in his British Patent No. 2675 of October 28, 1864, "PREPARING COMPOUNDS OF GUNCOTTON AND OTHER SUBSTANCES," he states that alcohol, treated in an analogous manner, may be substituted for wood alcohol. Now both of these alcohols gelatinate pyroxylin, so the dissolving power of camphor was not disclosed. Spill, who was a keen observer, noted that it was possible to use moist pyroxylin, as may be gathered from several of his patents, and drew the conclusion that in certain combinations the employment of anhydrous alcohols was not essential. In his British Patent No. 2,666 of September 21, 1867, "TREATING XYLOIDINE," he gives us the important solvent commercial grain alcohol mixed with benzol. Two years later, British Patent No. 3,102 of October 26, 1869 and U. S. Patent 97,454 of November 30, 1869, he published

his famous formula of a solution of camphor in commercial grain alcohol, and this formula and this disclosure are and have been the foundation of the celluloid industry. Spill's process of gelatinating pyroxylins by means of this solvent and masticating the pasty mass between rolls is and has been the process followed by celluloid manufacturers all over the world, Hyatt and his backers included, and not the visionary, inoperative process of U. S. Patent 105,338 of July 12, 1870, granted to John W. Hyatt, Jr., and Isaiah S. Hyatt. The patent covering this alleged invention was several times re-issued, exalted to the state of a fetich, and made an instrument of the most oppressive patent litigation. Hyatt disclaims the use of alcohol, but in practice cannot do without it. What his actual knowledge was, is best evidenced by this quotation from the text of 105,338:

"The product is a solid about the consistency of sole leather, but which subsequently becomes as hard as horn or bone by the evaporation of the camphor. Before the camphor is evaporated the material is easily softened by heat, and may be molded into any desirable form, which neither changes nor appreciably shrinks in hardening.

"We are aware that camphor made into a solution with alcohol or other solvents of camphor has been used in a liquid state as a solvent of xyloidine. Such use of camphor as a solvent of pyroxylin we disclaim."

In passing, I may remark that the step of the first claim "Grinding pyroxylin into a pulp" was published in British Patent No. 2,249 of September 15, 1860, granted to Stephen Barnwell and Alexander Rollason.

That Hyatt experienced great difficulty in circumventing Spill's patents and in fact did not succeed, does not constitute him the inventor of the pyroxylin-camphor compound which Spill first made, and which is made to-day by Spill's original method.

The decision that the step taken by Spill was too short to entitle him to a patent may have appeared very obvious in 1884, especially to his rivals, but I am of the opinion that it was a tremendous leap forward in 1869. But whichever way one may view this decision, it does not establish that Hyatt was the inventor of celluloid, the material, not the trade mark, nor that Hyatt's process is the one used in the industry. Rather the reverse, it says that anybody may use Spill's process, Hyatt's backers, the defendants in this suit, included.

Considering the exceptional opportunities which Prof. Chandler has enjoyed to acquaint himself with the real processes and the history of the celluloid industry, nothing could be less defensible than the use he tries to make of Spill's British Patent 1,739, of May 11, 1875. For the benefit of unbiased readers, I append herewith a circular of the Xylonite Company, Limited, bearing date of March 31, 1871, which shows better than anything else what had been accomplished at that early date:

THE XYLONITE COMPANY LIMITED

MANUFACTORY: HACKNEY WICK, LONDON, N. E.

Mr. D. Spill, Manager

XYLONITE: a substitute for Ivory, Bone, Horn, Tortoiseshell, Hard Woods, Vulcanite, Papier Maché, Marbles, Brass, and Veneers for Cabinet Work. It is also applied to Waterproofing Fabrics, Leather, Cloth, Book Binders' Cloth, Card Cloth, Writing Tablets, Bagatelle Balls and Pianoforte Keys, Gear and Friction Wheels, and Bearings for Machinery, Spinner's Bosses, Tubing; and as an Insulator and protector of Telegraph Wires.

It may be embossed, turned, polished, and worked in the same manner as the substances above named; is not affected by chemicals, or atmospheric changes, and is, therefore, valuable for shipment to hot climates.

It is also applicable to Photographic purposes, *viz.*, as windows for the Dark Room, for which the material is chemically prepared so as to arrest the actinic rays of light. It can also be spread upon fabrics for the purpose of Field Tents, thus avoiding the use of colored glass windows; and lastly, differently prepared, is a substitute for glass plates for Negatives, it having

[1] THIS JOURNAL, 6 (1914), 156–158.

the advantages of being light, flexible, and durable, and perfectly strictureless.

INSTRUCTIONS TO SURFACE AND POLISH XYLONITE SHEET

The Surface of the sheet can be made smooth with either a file, glass paper, scraper, or plane; or by grinding on a stone, either with fine emery powder and water, fine emery powder and oil, or pumice stock and water; it may also be pressed to a smooth surface between polished plates of metal heated to about 212 degrees Fahrenheit.

Polish with oil and crocus, oil and rotten-stone, or oil and whiting, combined with friction; it may also be French polished, in the same manner as cabinet work or hard woods.

The friction polish is most durable, and may be obtained by the use of a rotary wheel or oscillating flat plate, having a leathern or woollen surface well supplied with the above-named polishing powders, combined with oil or water. Finish with a rotating or oscillating brush or wheel made of hair, cotton or wool, well supplied with whiting combined with oil or water.

INSTRUCTIONS FOR WORKING AND FASTENING HANDLES

To work Xylonite Handles for Table or Pocket Cutlery, the material should be first surfaced or shaped, either with a hardened steel file, or by grinding upon "fine grit" stones, supplied with water in any convenient way; then polished on a leather surfaced or buff wheel, well supplied with rotten-stone and oil, or powdered pumice stone, and oil; and finished on a rotating dolly or wheel composed of hair, cotton, woollen rays, or felt, well supplied with whiting combined with oil or water. This will give a high gloss, similar to ivory.

In many instances the ordinary method of polishing ivory will suffice.

Previous to working Xylonite into Table or Pocket Knife Handles, in large practice, it is desirable, in order to avoid the possibility of the warping or contortion of the material, that the article should be shaped approximately to its finished form, either by file or grinding; the hole drilled for the tang; and the rough handle then seasoned and set, by exposing it for from 14 to 21 days to a warm and free atmosphere of about 100 to 130 degrees Fahrenheit. After this it may be surfaced and polished.

Xylonite may be moulded into form under combined pressure and heat. The mould and material should be heated to about 212 degrees Fahrenheit, pressure then applied, and the mould allowed to remain until cool, or it may be plunged instantly into cold water, in order to set the shape quickly.

To permanently fasten Xylonite Handles, which will not be affected by climate or boiling water, and do not require pinning or riveting:

Heat the tang of the blade in a gas flame to about 300 degrees Fahrenheit, or, say a blue heat.

Fill the drill hole of the handle with flour of sulfur or powdered brimstone, then insert the hot tang; this will melt the powder, the excess of which will escape while adjusting the handle; in a few seconds the tang will be sufficiently cool for the handle to become firmly set. Half a dozen tangs may be heated at one time by an ordinary gas flame at the workman's bench in about one minute, thus economizing time, avoiding the inconvenience and risk of fires, and the use of the melting pot.

If necessary to remove handles from the tang, hold the blade firmly in a vice, then with a lever or spanner forcibly twist the handle round, at the same time pulling it off; this may be executed without injury to the article.

Knives having Xylonite handles fastened as above described may be cleaned with boiling water without risk of becoming cracked, discolored, loose on the tang, or injured in any way, as neither the material nor the fastening will be affected by heat considerably above the temperature of boiling water.

The ordinary fastenings with Rosin will not answer with Xylonite handles.

<div align="right">7, GREAT WINCHESTER STREET BUILDINGS, E. C.
LONDON, 31st March, 1871</div>

GENTLEMEN:

I beg to inform you that this Company has appointed Messrs. BEACH & Co., of Hartford, Connecticut, the sole Agents for the United States of America and Canada.

You will, therefore, oblige by forwarding to them your orders for the future, which will receive prompt attention.

Messrs. Beach & Co. will have the pleasure of affording you full particulars of the various uses of our material, together with Price Lists, etc.

I am, Gentlemen, Yours obediently,

<div align="right">HERBERT J. CANNING, *Secretary*</div>

Tons of Spill's xylonite were at this time imported into this country. Worden's description ("Nitrocellulose Industry," pp. 571, 572) of Spill's work is incomplete. His criticism of Parkes' processes (*Ibid.*, p. 568, foot-note) does not tally with the facts.

In regard to the dehydration of pyroxylin by means of alcohol, Mr. Hyatt labors under a misapprehension. This process is about as old as collodion itself, and was first patented by Cutting in 1845. It was first employed in an industrial way by J. R. France, the late President of the Arlington Company (died in 1895), and when his company was sued for infringement

of the Hyatt alcohol dehydration patent, it took only one hearing to cause a discontinuance of the suit.

The invention of celluloid has been discussed[1] before in a manner sufficiently lucid to cause anybody not possessed of the light-heartedness of Prof. Chandler and Dr. Baekeland to make a little more sure of his premises. I think I gave Mr. Hyatt due credit in the article which Prof. Chandler takes exception to, as I also did in 1895, when I said:

"In the United States, J. A. McClelland and John W. Hyatt were at work to utilize the valuable properties of soluble pyroxylin. But an invention overshadowing all the others in importance was made by Daniel Spill in 1869, when he first produced a pyroxylin-camphor composition, plastic at about $75°$ C., by gelatinizing pyroxylin by means of a solution of camphor in commercial grain alcohol. As far as the chemical side is concerned, Daniel Spill must be hailed as the father of the celluloid industry, while to John W. Hyatt, at that time of Albany, N. Y., the greatest credit is due for devising suitable machinery for the intricate processes involved, for discerning the importance of pure materials, and for the perseverance which he exhibited under most adverse conditions."

It would have been much better to have the presentation of the Perkin medal to Mr. Hyatt based on the things which he accomplished, of which there are a good many.

<div align="right">ROBERT C. SCHÜPPHAUS</div>

175 PEARL STREET, NEW YORK
March 27, 1914

LABORATORIES IN THE CHEMISTS' BUILDING

The Chemists' Building Company, organized primarily to finance the construction and operation of a building in which to house The Chemists' Club and various Chemical Societies in New York City, starts on May 1st next, a new form of leases for its tenants.

There has been a good demand for laboratories in the Chemists' Building and only a few of them are left. They rent at a uniform rate of $2.00 per square foot per annum. Each laboratory has its own gas supply and meter. Heat, electric light, water, compressed air and vacuum are supplied by the building. Laboratories have openings for hood connections. The Chemists' Building is most conveniently located at 50 E. 41st Street close to the Grand Central and Subway Stations.

The Chemists' Club acts as agents for the Building Company, and all inquiries may be addressed to the House Committee or the Superintendent of the Club.

AN INVESTIGATION OF THE PRESENCE OF FURFURAL IN CIDER VINEGAR—A CORRECTION

Through an oversight the final paragraph of the article under the above title in THIS JOURNAL, 6, 214, was omitted. It follows: "The vinegars used above, except the farmers' vinegars, were made under the direction of Asst. Prof. H. Louis Jackson for his study of pure cider vinegar. The test for furfural was made at his suggestion."

<div align="right">AGNES A. ANDERSON</div>

STATE FOOD LABORATORY
UNIVERSITY OF KANSAS, LAWRENCE
April 13, 1914

CORRECTION

The articles on "Sociological Work of the New Jersey Zinc Company" by F. Hughes, "Welfare and Safety Provisions at the Welsbach Company's Plants" by H. Lyon, THIS JOURNAL, 6, 333 and 336, were presented at the JOINT MEETING of the New York Sections of the American Chemical Society, The Society of Chemical Industry and the American Electrochemical Society, Dec. 12, 1913, and not at the Annual Meeting of the American Institute of Chemical Engineers as stated in the foot-notes.

[1] Schüpphaus, *Jour. Soc. Chem. Ind.*, **14** (1895), 557 and **26** (1907), 383; Joyce, THIS JOURNAL, **3** (1911), 194 and 702.

PERSONAL NOTES

Sir Ernest Rutherford, F.R.S., of the University of Manchester, England, spoke before the National Academy of Sciences, April 21st, 22nd and 23rd on "The Constitution of Matter and the Evolution of the Elements." This is the beginning of a series of lectures covering several years and designed to give a clear and comprehensive outline of the broad features of inorganic and organic evolution in the light of recent research. The expenses of this series are taken care of by the William Ellery Hale Foundation, made in memory of the late William Ellery Hale of Chicago.

The Columbia University Commencement this year takes the form of a celebration of the 50th Anniversary of the founding of the School of Mines. An especial feature will be the Inauguration of the Chandler Lectureship and the Award of the Chandler Medal on May 29th. The first Chandler Medal will be awarded to Dr. Leo. H. Baekeland.

A portrait of Sir William Ramsay, painted by Mr. Mark Milbanke, has been presented to University College, London, by former colleagues and past students. Prof. J. Norman Collie made the address. A replica of the portrait has been presented to Lady Ramsay.

The Pratt Institute Chemical Alumni Association of Brooklyn held their 16th Annual Reunion and Dinner at the Hotel Gregorian on the evening of April 16th. The dinner was well attended and brought together graduates of the three-year evening course for the last eleven years. Reports from various members showed that many responsible positions are being filled by graduates of the Institute. Arthur S. Somers acted as Toastmaster. Dr. W. R. Whitney of the General Electric Co talked interestingly on the research that led up to the production of the metal filament incandescent lamp. Dr. S. G. Rogers, Medical Inspector of the N. Y. State Department of Labor, told how they were trying to render labor more efficient by improving sanitary conditions. Other speakers were: District Attorney James C. Cropsey of Kings County, Geo. A. Hitchcock, Samuel S. Edmonds of Pratt Institute and Arthur F. Wiehl. All the past presidents of the Association were seated at the head table with the guests of the evening. The officers for the coming year are: Arthur F. Wiehl, *President;* Harry W. Lange, *Vice-President;* Irving A. Schumann, *Secretary-Treasurer;* A. J. Farry, Harry J. Bloom, Wm. J. Bedell and G. Clarence Woolley, *Directors.*

Dr. Max A. Kunkler, research chemist for The Joslin-Schmidt Co. of Cincinnati, died March 29th at the age of 26.

On March 28th the members of the "Round Table" at the Bearon Café, New York City, gave a luncheon to their honored member, Adolf du Faur, commemorating the 88th anniversary of his birth. Chemists, Mining Engineers, Metallurgists and Chemical Merchants meet daily for luncheon at the "Round Table" which is known the world over. The luncheon was under the direction of Dr. Hugo Schweitzer, who, in the name of the "Stammtisch," delivered an address of congratulation in German. Dr. Emil Schill then presented Mr. du Faur with an engrossed certificate of honorary membership (the first awarded) in the N. Y. Section of Verein Deutscher Chemiker. Mr. du Faur responded, acknowledging his pleasure at the honor accorded him. Among those present were: F. A. Schütz and F. F. Schütz, Jr., son-in-law and grandson of Mr. du Faur; Emil Schill, E. A. Widmann, H. C. A. Seebohn, H. Lieber, T. J. Parker, T. B. Wagner, E. Bilhuber, F. Stobaeus, Aston and Karl Eilers, Mr. Fohr, Willard P. Ward, Theo. Geisenheimer, Carl Beckmann, H. C. Schüpphaus, Bernhard C. Hesse, L. Saarbach, F. de Jahn and many others.

Mr. Faber du Faur was born March 27, 1826 in Wasseralfinger, Wurtemberg. He attended the Polytechnicum in Stuttgart and studied chemistry under Fehling. His faithfully kept college diary was presented by him to the Library of The Chemists' Club. He landed in the United States, Jan. 1, 1851, where as a Mining Engineer and Patent Attorney he has led an active and eventful life. Among his numerous inventions, for which he was granted valuable patents, the Tilting Furnace, invented in the early sixties and still in common use deserves especial mention. During the Civil War, he served as Adjutant to General Meigs and as Captain of Engineers was entrusted with the task of fortifying and defending Washington.

Dr. N. Edward Loomis, Assistant Professor of Chemistry at Bowdoin College, Brunswick, Maine, has recently been called to take charge of the newly organized Department of Physical Chemistry at Purdue University, Lafayette, Indiana.

G. H. P. Lichthardt, Analyst of the Sacramento Department of Health, calls attention to a new adulterant which he has found in Ice Cream Cones. These yielded 0.50 and 0.45 per cent of strongly alkaline ash which had a silica content of 50 and 47 per cent. Inspection of the manufacturing plant showed that water glass solution was being used, acting, no doubt, as a preservative and allowing the use of a thin batter in making up the cones.

On April 15th, the reorganizers purchased the property of the American Water Works & Guarantee Co. at the receiver's sale. The consideration was $1,250,000.

The Connellsville, Pa., coke production, which has been around 350,000 tons weekly, is being materially curtailed. During the middle of April, the Frick Company closed 1,300 ovens, and it was reported that other interests had shut down many ovens. The number of ovens in operation for an output of 350,000 tons per week (9,700 cars) is 27,000.

The Itinerary of the Annual Chemical Inspection Trip for Advanced Chemistry and Chemical Engineering Students of the University of Illinois included visits to the following plants in and near Chicago: Universal Portland Cement Co., Buffington, Ind.; Indiana Steel Company; The By-Product Coking Plant; Illinois Steel Co.; Standard Oil Refinery, Whiting, Ind.; Grasselli Chemical Co.; U. S. Metals Refining Co.; American Smelting & Refining Co.; Sherwin-Williams Co.; Armour & Co. Soap Works; Peoples' Gas, Light & Coke Co.

The American Manganese Manufacturing Co., which is in possession of a large deposit of manganese ore in Minnesota, proposes to produce ferro-manganese at the plant of the Dunbar Furnace Co., Pittsburgh, Pa.

Sir Ernest Rutherford of Manchester, England, lectured on "Recent Advances in Radioactivity" on April 18th under the auspices of the Columbia University Department of Physics. In substance the lecture was the announcement of the following conclusions drawn from recent experiments as yet unpublished: (1) Absolute proof that the α-particles projected from radioactive substances are helium atoms. (2) Experiments studying the scattering of the α-rays by matter show that positive electrons are excessively concentrated, even more so than the negative ones. (3) The charge on the nucleus of an atom is proportional to the atomic weight of the element. (4) Study of the "magnetic spectra" of radioactive elements indicates that the escape of β-particles from the nucleus of an atom starts a radiation that is the γ-radiation and that is the characteristic mode of vibration of that particular kind of atom. (5) Further studies of the γ-radiation lead to the conclusion that the charge on the nucleus of an atom controls its properties; *i. e.,* that elements of different atomic weights may have identical properties, *e. g.,* Radium B and lead have the same "magnetic spectrum" as reflected from rock salt crystals.

GOVERNMENT PUBLICATIONS

By R. S. McBride, Associate Chemist, Bureau of Standards, Washington

NOTICE.—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these consular reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

HOUSE OF REPRESENTATIVES

Radium—Report from Committee on Mines and Mining favoring House Bill No. 12741, which is intended "to provide for and encourage prospecting, mining, and treatment of radium-bearing ores in lands belonging to United States, for purpose of securing adequate supply of radium for government and other hospitals in United States," dated February 3, 1914. (18 pages; paper, 5c.) In this connection House Joint Resolutions 185 and 186 and Senate Bill 4405 and the hearing reports on them, are of interest. These latter are not published for general distribution, but can be secured from members of Congress in some cases

STATE DEPARTMENT

Transactions of 15th International Congress on Hygiene and Demography. Edited by the Secretary General. 6 Vols., 9 parts. Complete report, with accompanying papers, of the sessions held in Washington, D. C., September 23–28, 1912. Not available for general distribution. Of value to those interested in hygiene, sanitation and allied subjects.

PATENT OFFICE

Official Gazette. Weekly publication for sale by Superintendent of Documents, $5 per year or 10c. per copy, in advance. Reports all patents granted and court decisions on patent cases; lists trademarks, designs, labels and prints at time when filed with office and announces their subsequent registration, when listing and registration are not simultaneous.

Classification Bulletin. 16 pp. Paper, 10c. Revised classification of subjects of invention, prepared by Classification Division for July 1 to Dec. 31, 1913.

BUREAU OF THE CENSUS

Report of the 13th Census. Volume X—Manufactures. 975 pp. Cloth, $1.25. The statistics of manufactures for certain selected industries were published as separate bulletins as rapidly as the statistics were compiled. These bulletins are now collected in the present volume, which is one of the eleven volumes constituting the full report of the 1910 census. The report for each industry gives data from operations in the calendar year 1909 of all establishments operating under the factory system, excluding "neighborhood, household, and hand industries." Some of the major classifications of the industries of chemical interest are the following: Textiles; metallurgical; electrical machinery and supplies; packing-house; dairy; canning; milling; starch and glucose; manufactured-ice; salt; sugar; general chemical and allied; bone, carbon, and lamp-black; dyestuffs; explosives; fertilizers; essential oils; acids; wood distillation; coke; gas; petroleum; soap; turpentine and rosin; leather; paper and pulp; clay products; and glass.

The large mass of data prevents review of the material presented; in general, there are statistics given on the following phases of each subject: General statistics, summary by geographical location, character of ownership, size of establishments, number of persons engaged, expenses, character of supplies and products, and values of each.

Data are given in detail for each state in addition to general summaries, and statistics for the metropolitan districts are also separately reported.

Separate bulletins are available in some cases, or the full set of reports may be consulted at libraries. An "*Abstract of the Census*" has also been prepared which is more convenient for general use. The section on *chemicals and allied industries* (other than those particular ones listed above) is obtainable as a separate paper for 15 cents.

Report of the 13th Census. Volume XI—Mines and Quarries. 369 pp. Cloth 65c. Statistics for mines and quarries similar to those outlined above for manufactures, being a general report and analysis. The most important mineral products are shown to be as follows, in order of value of product for year 1909: Bituminous coal, natural gas, anthracite coal, iron, copper, precious metals, limestone, lead and zinc, granite and trap-rock, sandstone, phosphate-rock, marble, slate, gypsum, sulfur and pyrite, clay, talc and soapstone, and mercury.

In addition to general summaries, there are detailed figures for each state; and elaborate reports on coal, iron, petroleum and natural gas are included.

INTERNAL REVENUE COMMISSIONER

Alcohol. Several reports and decisions on alcohol have appeared recently from this office, as follows:

Regulations and instructions relating to manufacture, redistillation and denaturation of domestic alcohol. Regulations 30 revised, supplement 2. 16 pp. Paper 5c.

Denatured alcohol, formula 2B, for especially denatured alcohol for use in manufacture of pyroxylin plastics. Treasury decision 1954. 4 pp.

Use of Mash fit for distillation in production of artificial wines. Treasury decision 1949. 2 pp.

GEOLOGICAL SURVEY

List of Publications. Circular No. 15 of the Superintendent of Documents office gives a recently revised list of all publications of the Survey.

Contributions to General Geology. Certain "professional papers" will each be made up of a number of short articles, and will form a series under the above title. The first of this series of articles are just out, published as separates from Professional Papers 85 and 90; the following two are included:

Resins in Paleozoic Plants and in Coals of High Rank. By David White. Professional Paper 85-E, 32 pp. Evidence is presented that anthracite and bituminous coals, as well as those of lower rank, originated as peats and in certain cases from resin-bearing plants. The significance of the relative resin content of coals is pointed out.

Geology of the Pitchblende Ores of Colorado. By E. S. Bastin. Professional Paper 90-A. 5 pp. A brief account of the occurrence of radium-bearing minerals in this district is given advance publication in this paper.

Mineral Resources of the U. S., Calendar Year 1912. Part I, Metals. 1079 pages; Part II, Nonmetals, 1218 pp. Statistics of the production, importation, and exportation of mineral substances in the United States, including accounts of the chief features of mining progress, comparisons of past and present production and conditions, and the application of the products in the useful arts. A consolidation of 63 advance chapters, each covering a single mining industry or group of allied industries. Among the chapters of chemical interest are those on: Abrasives; borax; gypsum; magnesite; phosphates; salt and bromine; bauxite and aluminum; gas, coke, tar and ammonia; precious and semi-precious metals (in several special districts).

Contributions to Economic Geology, 1912. Part I, Metals

AND NONMETALS EXCEPT FUELS. Bulletin 540. 563 pp. This bulletin is made up of 30 brief reports on such investigations of mineral deposits as have a direct economic bearing; separate copies of the reports are available in most cases. Topics of pure geological or mineralogical interest are not taken up. Each report deals with certain minerals or ores for one district only. Among the subjects so treated are: deposits of gold, copper, lead-silver, iron, titaniferous magnetite, alunite, granite, marble, clay, phosphates, potash and other salines, salt and borax, sodium sulfate, borates, niter, sulfur, magnesite, celestite, and diamond-bearing peridotite.

PART II, FUELS. Bulletin 541. This section is not yet complete, although some separates have appeared.

BUREAU OF MINES

Fuel Briquetting Investigations, July, 1904 to July, 1912. By C. L. WRIGHT. Bulletin No. 58, 277 pp and 21 plates. Paper 45c. This bulletin reports the results of fuel briquetting begun under the U. S. Geological Survey in 1904 and continued at various places until July, 1912. Results previously reported in government publications as well as new information are assembled in the present bulletin. The condition of the briquetting industry, costs, machinery used, and fuels available for use in this work are discussed. A large amount of tabular data are given, including: results of analyses, physical tests and combustion experiments on the fuels, binders and briquets of different sorts. Detailed data for many coals and lignites are reported.

The Sampling and Examination of Mine Gases and Natural Gas. By G. A. BURRELL and F. M. SEIBERT. Bulletin No. 42, 116 pp. and 2 plates. Paper 20c. The subject matter is arranged under principal headings among which are the following: Collection of samples of mine gases; determination of moisture; apparatus and methods used (for air analysis, determining CO_2, CO, H_2, N_2, and CH_4); apparatus used in analyzing other gas mixtures (such as illuminating gases); detection of carbon monoxide (by mice and birds); determination of oxides of nitrogen in mine air; use of the gas interferometer; and apparatus for analyzing natural gas. A large amount of old material is included from former reports of this Bureau and other sources, but experimental results from recent work and extended discussion of the various methods are also given. Much of the material would be of value to a person interested only in artificial gas or air analysis, both in regard to apparatus and methods.

Petroleum Technology. A new sub-series in the bulletins of this Bureau is given this title; this sub-series is made up, as is the sub-series on "mineral technology," of bulletins numbered serially as a part of the full list of the bulletins.

Permissible Explosives. By CLARENCE HALL. Technical Paper No. 71. 12 pp. Paper 5c. A list of all explosives found by tests previous to January 1, 1914, to conform to rules of the Bureau of Mines. (See earlier publications of this Bureau for full reports on methods of testing and proper storage and handling.)

Metal-Mine Accidents. Compiled by A. H. FAY. Technical Paper 61. 74 pp. Paper, 10c. Classified statistics for operations of 1912, showing causes and distribution (both geographic and by character of mine) of accidents.

Mud-laden Fluid Applied to Well Drilling. By J. A. POLLARD and A. G. HIGGIN. Technical Paper 66. 20 pp. A proposed method for gas and oil-well drilling is described, by which wells may be drilled and the oil recovered without waste of the gas which accompanies it. This is an important matter where gas is struck when there is immediate commercial demand only for oil.

Production of Explosives in the U. S. Compiled by A. H. FAY. Technical Paper 69. 7 pp. The total production of explosives during 1912 was reported as follows:

	POUNDS
Black Powder	230,233,369
Permissible explosives	24,630,270
"High" explosives (dynamite nitroglycerine, dynalite, guncotton, etc.), other than permissible explosives	234,469,492
TOTAL,	489,333,131

The locality and purpose of use are shown by full data; utilization is accompanied by an average of 0.59 fatalities per 1,000,000 lbs. of explosive used.

Relative Effects of Carbon Monoxide on Small Animals. By G. A. BURRELL, F. M. SEIBERT and I. W. ROBERTSON. Technical Paper 62. 23 pp. Paper 5c. Of value in study of mine-accident prevention.

BUREAU OF STANDARDS

Copper Wire Tables. Circular No. 31, 2nd Edition. 70 pp. This circular with its tables was prepared at the request and with the coöperation of the standards committee of the American Institute of Electrical Engineers. The data on which the tables are based were formally adopted as international copper standards by the International Electrotechnical Commission in September, 1913. Tables, accompanied by full discussion, give the resistivity, temperature coefficient and density of annealed copper, comparison of wire gages, data for copper-cable and aluminum-wire resistivities, etc.

Testing of Barometers. Circular No. 46. 12 pp. The characteristics of barometers suitable for various uses are given, and the limitations of each type briefly indicated. A description is included of the tests made by the Bureau of Standards in the calibration of mercury or aneroid barometers and instructions are given regarding application for tests and fees charged. The fees vary from $10 for a determination of the gas correction or a calibration with high accuracy, to $2 for test at one point on a common barometer with ordinary accuracy. Fees for tests on aneroids vary with character of test and number of instruments submitted.

The Testing of Mechanical Rubber Goods. Supplement to Circular of this name, which is No. 38. 16 pp. Preliminary report and recommendations of Joint Rubber Insulation Committee for specifications for rubber compounds and for the procedure for analysis of rubber compound. These specifications are adopted as tentative for one year's trial by the Committee. A model specification for 30 per cent Hevea rubber compound is also proposed in preliminary form. (The original circular No. 38 deals largely with the processes of manufacture and mechanical testing of rubber goods.) [See THIS JOURNAL, 6, 75.]

Testing of Hydrometers. Circular 16, 3rd edition. 16 pp. A revision of the Bureau's hydrometer specifications, instructions for the use of hydrometers, description of methods and statement of fees for testing them.

Standard Specifications for Incandescent Electric Lamps. Circular 13, 6th edition. 20 pp. Revised specifications used by the U. S. Government in lamp contracts and proposed as suitable for general use by other purchasers.

Bulletin, VOL. 9, No. 4, and VOL. 10, NOS. 1 and 2 have come from press since January 1st. These include the following scientific papers, each of which are obtainable as separates:

(1) **A Micropyrometer.** By G. K. BURGESS. Scientific Paper 198. 4 pp. The microscope and pyrometer used for melting-point determinations on minute specimens of metals, etc., are combined in one instrument to enable a single observer to watch the melting and to make the temperature measurement.

(2) **Melting Points of the Refractory Elements.** I—Elements of Atomic Weight from 48 to 59. By G. K. BURGESS and R. G. WALTENBERG. Scientific Paper 205. 14 pp. Micropyrometric measurements of the melting points in hydrogen of these elements gave the following results: Ni 1452 ± 3;

Co 1478 ± 5; Fe 1530 ± 5; Mn 1260 ± 20; Cr 1520 to greater than Fe; Va 1720 ± 20; and Ti 1794 ± 12.

(3) **Simplified Formula for the Change in Order of Interference Due to Changes in Temperature and Pressure of Air.** By I. G. PRIEST. Scientific Paper 199. 4 pp.

(4) **New Calorimetric Resistance Thermometers.** By H. C. DICKINSON and E. F. MUELLER. Scientific Paper 200. 10 pp. A new form of electrical resistance thermometer having small lag and numerous advantages for use in high precision calorimetric work.

(5) **The Silver Voltameter. Part III.** By E. B. ROSA, G. W. VINAL and A. S. McDANIEL. Scientific Paper 201. 60 pp. Reports the second series of quantitative experiments and the preparation and testing of silver nitrate for this work. (Previously abstracted in *C. A.*)

(6) **Note on Cold-Junction Corrections for Thermocouples.** By P. D. FOOTE. Scientific Paper 202. A discussion of the importance and method of making this correction; omission of the correction may cause errors as great as 50° C.

(7) **Latent Heat of Fusion of Ice.** By H. C. DICKINSON, D. R. HARPER 3d, and N. S. OSBORNE. Scientific Paper 209. 31 pp. Measurements by two independent methods in a precision calorimeter on 92 samples of 100 to 500 grams of ice from various sources give results agreeing within 1 part in 1000. The mean of the final 21 determinations on samples of "plate," "can" and "natural" ice gave for the latent heat of fusion 79.63 calories (15°) per gram mass, equivalent to 143.3 B. t. u. per pound mass or to 143.5 B. t. u. per pound weighed in air against brass or iron weights.

(8) **Melting Points of Some Refractory Oxides.** By C. W. KANOLT. Scientific Paper 212. 18 pp. Measurements in a graphite resistance furnace, using an optical pyrometer; the results reported are as follows:

Oxide	M.P.	Supporting material
Cr_2O_3	1990°	Tungsten, graphite
Al_2O_3	2050°	Tungsten, graphite
CaO	2572°	Tungsten, CaO
MgO	2800°	Graphite

Special Studies in Electrolysis Mitigation. By E. B. ROSA and B. McCOLLUM. Technologic Paper 27. 55 pp. A report on the preliminary study of conditions in Springfield, Ohio, with recommendations for mitigation. The results are presented for this one case, but the principles laid down can be taken as of general interest and value.

Viscosity of Porcelain Bodies. By A. V. BLEININGER and PAUL TEETOR. Technologic Paper 30. 11 pp. As a measure of viscosity the deformation under tensile strain was used at temperatures from 1060° to 1310°. Tabular results and curves are given.

DEPARTMENT OF AGRICULTURE

Agriculture Bulletins. Publications of bulletins and circulars by the bureaus of the Department of Agriculture has been discontinued; all such contributions (from bureaus of Chemistry, Soils, Animal Industry, Plant Industry, etc.) will hereafter be published in the new series of Bulletins issued from the office of the Secretary of Agriculture and called "Agricultural Bulletins."

Journal of Agricultural Research. Monthly, free only to certain libraries and institutions generally on exchange. Annual subscription price $2.50 per volume of 12 numbers, payable in advance to the Superintendent of Documents. The numbers of this year have thus far contained the following articles of chemical interest:

(1) **Environmental Influences on the Physical and Chemical Characteristics of Wheat.** By J. A. LeCLERC and P. A. YODER.

(2) **Presence of Some Benzene Derivatives in Soils.** By EDMUND C. SHOREY.

(3) **Crystallization of Cream of Tartar on Fruit of Grapes.** By WILLIAM B. ALWOOD.

(4) **Reduction of Arsenic Acid to Arsenious Acid by Thiosulfuric Acid.** By ROBERT M. CHAPIN.

A Special Flask for the Rapid Determination of Water in Flour and Meal. By JOHN H. COX, Asst. in Grain Standardization, Bureau of Plant Industry. Agricultural Bulletin 56. 7 pp. Paper 5c. Simple description and directions for use of this flask in flour and grain testing.

Tests of the Waste, Tensile Strength, and Bleaching Qualities of the Different Grades of Cotton. By N. A. COBB, Agricultural Technologist, Bureau of Plant Industry. Agricultural Bulletin 62. 8 pp. Paper 5c. A preliminary report on milling tests of interest in cotton-mill work.

Manufacture of Flavoring Extracts. By E. M. CHACE. Reprint (new edition) from yearbook of 1908. 10 pp. Paper 5c.

Respiration Calorimeter and Results of Experiments with It. By C. F. LANGWORTHY and R. D. MILNER. Reprint (new edition) from Yearbook of 1910. 12 pp. Paper 5c.

Giant Kelps of the Pacific Coast as a Source of Potassium Salts. By F. K. CAMERON. Bureau of Soils. An extended report on this subject is ready for press; it will be accompanied by maps of the kelp beds and includes recommendations as to the utilization of the new source of potassium for use as a fertilizer.

List of Publications. Circular 40 of Superintendent of Document Office is an alphabetical subject list of the bulletins and circulars of the Bureau of Chemistry and of the published proceedings of the annual conventions of the A. O. A. C., so far as they are now in stock.

Methods of Food Analysis. This Bulletin (No. 107 of Bureau of Chemistry), which gives the official and provisional methods for food analysis of the A. O. A. C., will be revised within a year; but another reprint of the current edition has been made and copies are to be had from the Superintendent of Documents for 20c.

CONSULAR REPORTS, MARCH

Ramie Fiber and its Manufacture. Description of the cultivation and manufacture of ramie fiber in China and Cuba and of the experiments toward its production in the Philippines. This material is mostly used for making "grass cloth" and paper, especially banknote paper. On account of its strength and resistance to moisture, ramie fiber is being used in one English factory as a substitute for hemp and flax. (Pp. 801–9.)

Alum Production of Shabin Kara Hissar. From 2000 to 3000 tons of alum are produced annually from natural deposits near this Turkish town. (P. 812.)

A new **Cement Factory**, with an annual production of 800,000 barrels is about to be erected in the Gori district of the Caucasus. (P. 825.)

Mineral Oil and **Natural Gas** have been reported from Marvaor, Nyitra County, Hungary. (P. 827.)

Iron Ore shipments from Korea in 1913 amounted to 135,263 tons, an increase of 3,000 tons over 1912. (P. 846.)

A **Soap** and **Candle Factory** started operations at Panama on Feb. 1, 1914. (P. 846.)

A **Seed-Oil Clearing House** has been established in Liverpool. (P. 875.)

Tests of **Para Rubber-seed Oil and Cake** showed that the oil has drying properties inferior to those of linseed oil and is not suited to the manufacture of linoleum, but can be used in making soft soap. Feeding experiments showed that the seed cake is suitable for feeding cattle, but not sheep. (P. 854.)

Colored Oil for Oleomargarine may be made from palm oil, which, when carefully prepared, has a high melting point (75°–100° F.) and has no disagreeable taste. (P. 875.)

The **Sulphate of Ammonia Industry** in Germany produced 500,000 metric tons in 1912, and 418,000 metric tons in 1911. Owing to competition between manufacturers in Bochum and in Ludwigshafen, the price is likely to decrease. (P. 878.)

Petroleum Fields in Bolivia are likely to be developed soon by two syndicates. (P. 879.)

Experiments on Electric Sparks and Mine Explosions in Wales, showed that sparks from a line at 9 volts (used in signaling) could not ignite an explosive atmosphere. (P. 879.)

Cement is manufactured in Haiphon (French Indo-China) and together with Coal and Zinc Ore formed the principal mineral exports. (P. 902.)

The principal Essential Oils exported from Hongkong to the U. S. and Europe are aniseed, cassia, and peppermint. (P. 906.)

BOOK REVIEWS

Molded Electrical Insulation and Plastics. By EMILE HEMMING. New York: Ward Clausen Co. 207 pages. Illustrated. Price, $3.00.

This a new book in the very meaning of the word since no treatise on that subject has heretofore appeared. The author by saying in the introduction—"a series of new inventions in the field of electrical insulation products have been developed and enormous progress has been made"—is fully justified, since practically a new industry has grown up in the manufacture of plastics and insulating materials, due to the remarkable progress made in the electrotechnical art and not the least due to the rapid development of chemistry also in this field within the last decade.

The reader, passing over in the book the very striking definition of molded insulation and the history of its development within the last ten years, finds himself transferred "in medias res," the curtain is raised and there is presented to the spectators' eyes a very intuitive and original classification of molded insulation products and plastics. How important a part in the manufacture of these compounds plays the proper selection of the raw materials is shown in the chapter, "Raw Materials," which surely will be of special interest to the chemist.

Articles like "Hydraulic Cement," "Shellac," "Formaldehyde," "Phenol," "Condensation," may be especially marked.

In the following chapters, dealing with the different classes of molded materials and describing the hot and cold molding processes, there are very instructive essays, e. g., "Ceramics," "Rubber Compounds," "Organic Plastics" (Celluloid Albuminoids) and "Synthetic Resinous Materials." The author gives a clear and full discussion of the properties of the molded materials as to life, puncture tests, mechanical strength, weather and heat-proof qualities, resistance to chemical action, etc., which shows the intimate knowledge and broad experience of the worker.

A feature of the book is the many illustrations of molded articles from properly composed plastic materials. The author shows how, by chemical synthesis, plastics have recently been produced, which have superseded a great many of the older insulating materials.

The chemist, chemical student, engineer and manufacturer will find in this book what has been done in the manufacture of plastics and insulating products and what is to be done yet to improve the qualities of these materials in order to fulfill the conditions necessary to produce a perfect insulator.

W. SANGER

Die Chemie und Technologie der Natürlichen und Künstlichen Asphalte. DR. HIPPOLYT KÖHLER. Zweite Vollstandig Umgearbeitete und Stark Vermehrte Auflage Herausgegeben von Dr. Hippolyt Köhler, Direktor der Rutgerswerke-Aktiengesellschaft, Berlin, und Dr. Edmund Graefe, Direktor der Duetschen Trinidad-Asphalt-Gessellschaft m.b.H., Dresden. 504+ xxi pages. Braunschweig, Verlag von Friedr. Vieweg & Sohn, 1913. Paper, $4.50.

This publication forms the 7th part of the "Neues Handbuch der Chemischen Technologie" which is being issued under the editorship of Dr. C. Engler. The first edition, by Köhler alone, appeared in 1904 and was a noteworthy compilation at that time. In associating with himself Dr. Edmund Graefe, Dr. Köhler has been enabled to bring the subject in essential particulars

up to date in a most satisfactory manner, especially as regards the uses of the native bitumens in the United States in the construction of pavements and roads, owing to Dr. Graefe's connection with the industry in this country and his intimate acquaintance with the processes which are being employed.

The contents of the book are divided into three parts: *First,* an historical consideration of the materials under consideration, the occurrence of the natural asphalts as known at the present time, the origin of bitumen and of asphalt, the physical and chemical properties, composition and components of asphalts, and finally, a chapter on "Artificial Asphalts" prepared from coal-gas tar, brown coal tar and from petroleum, as well as reference to oil-gas tar, water-gas tar, montan pitch, the pitches obtained in the saponification of the fats and resin pitches.

The Second, or technical part, is descriptive of the industries in which asphaltic materials are used, structurally for pavements, roads and water-proofing, and industrially in the preparation of roofing felts and water-proofing papers, as well as for insulating material. Attention is also called to the uses of asphalt in rubber substitutes, in varnishes and cementing materials, in the formation of tubes, cork asphalt, as an insulating material and in photographic processes.

The Third, or analytical part, summarizes very thoroughly the physical and chemical methods in use in the investigation of the natural and so-called artificial asphalts, and the technical testing and examination of asphaltic materials of all descriptions.

The book is a compilation of the results of practically everything that has been done in all parts of the world, in the study of the solid native bitumens and their surrogates, both as to their occurrence, nature and origin, and their applications in all of the industries. The data have been assembled with that thoroughness and detail which is characteristic of books of this type which are published in Germany. It can be criticized only because it is too thorough in this respect, and includes much material which the exercise of good judgment might have eliminated as being of doubtful value. Looked at from any point of view, the book is a monumental one, and will be found of the greatest value in the hands of any one who can make use of the German language, and it can be highly recommended to all who are interested in the subject of which it treats. The new edition contains 504 pages as compared with the 433 of the first edition.

CLIFFORD RICHARDSON

Solvent Oils, Gums, Waxes and Allied Substances. F. H. HYDE. D. Van Nostrand Company, New York. $2.00.

This book is a very short compilation of the chemical and physical properties of the above substances. It includes some of the more common methods of analysis and tests for oils and fats and concludes with chapters on alkaloidal substances, bitter principles and various miscellaneous substances.

Such a conglomeration condensed to 170 small pages must necessarily be of very limited value.

The chapter on proteins which the author labels "Albumenoids or Proteids" is particularly antiquated.

SIDNEY BORN

Practical Science for Engineering Students. BY H. STANLEY. Published by Methuen and Company, Ltd., 36 Essex Street, Strand, W. C., London. Price, $0.75.

This book was written, according to the author, "primarily

to suit the needs of evening students who have passed the very elementary stages. It should also be useful, it is hoped, to those entering on an engineering training proper, who have not gone through a good course of laboratory work."

In the opinion of the reviewer, while the book contains some good information, the treatment, though clear, is so superficial that it is likely to mislead the beginner for whom it is primarily written. The tables of constants do not, in many cases, contain the latest values.

G. V. Wendell

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian The Chemists' Club, New York

Carbohydrates, Short Handbook of the. By B. Tollens. 3rd Ed. 8vo. 816 pp. Price, $5.50. J. A. Barth, Leipzig. (German.)

Catalysts, The Biochemical, in Life and in Industry. By Jean Effront. 8vo. 772 pp. Price, $5.00. Dunod & Pinat, Paris. (French.)

Chemistry and Its Borderland. By Alfred W. Stewart. 8vo. Price, $1.25. Longmans, Green & Co., New York.

Chemistry, General, Physical and Theoretical, Textbook of. Vol. I. By W. Kuester and A. Thiel. 2 Vols. L. 8vo. Price, $4.75. Carl Winter, Heidelberg. (German.)

Chemistry, Scientific, Progress of, in Our Own Times. By William A. Tilden. 2nd Ed. 8vo. 366 pp. Price, $2.25. Longmans, Green & Co., New York.

Cotton, Its Origin, Use, History and Significance. By Karl Steuckart. 8vo. 59 pp. Price, $1.00. Bernhard F. Voigt, Leipzig. (German.)

Engineering, Chemical, Notes on. By J. W. Hinchley. 8vo. J. & A. Churchill, London.

Factory Organization and Administration. By Hugo Diemer. 8vo. 370 pp. Price, $3.00. McGraw-Hill Book Co., New York.

Fibers, Spinning Animal and Mineral. By D. de Prat. 8vo. 482 pp. Price, $1.75. L. Mulo, Paris. (French.)

Fuel, Solid, Liquid and Gaseous. By J. S. S. Brame. 8vo. 372 pp. Price, $3.25. Edward Arnold, London.

Metal Coloration and its Production. By G. Buchner. 5th Ed. Lex. 8vo. 426 pp. Price, $2.25. M. Krayn, Berlin. (German.)

Metallic, Inter-, Compounds. By C. H. Desch. 8vo. 116 pp. Price, $0.75. Longmans, Green & Co., New York.

Organic Compounds, Chemical, Technology of. By R. O. Herzog. 8vo. 732 pp. Price, $5.50. Carl Winter, Heidelberg. (German.)

Physics, Molecular. By J. A. Crowther. 8vo. J. & A. Churchill, London.

Plastics, Molded Electrical Insulation and. By Emile Hemming. 8vo. Price, $3.00. Ward Clausen Co., New York.

Refrigeration, Mechanical. By H. J. Macintire. 8vo. 346 pp. Price, $4.25. Chapman & Hall, London.

Silk, Raw. By L. Duran. Cr. 8vo. Price, $2.75. Spon & Co., London.

Sugar Industry, Chemistry of the. By Oskar Wohryzek. 8vo. 160 pp. Price, $5.00. Julius Springer, Berlin. (German.)

Tanning Laboratories, Chemical, Handbook for. By Georg Grasser. L. 8vo. 400 pp. Price, $3.75. Schulze & Co., Leipzig. (German.)

Viscosity of Liquids. By A. E. Dunstan and F. B. Thole. 8vo. 92 pp. Price, $0.90. Longmans, Green & Co., New York.

Water Purification, Modern Methods of. By J. Don and J. Chisholm. 8vo. 398 pp. Price, $4.20. Longmans, Green & Co., New York.

RECENT JOURNAL ARTICLES

Acids, Mineral, Report on the, Industry in 1913. By K. Reusch. *Chemiker Zeitung*, Vol. 38, 1914, No. 36, pp. 385–386.

Alloys, Non-Ferrous, Nomenclature of. Anonymous. *Industrial Engineering*, Vol. 14, 1914, No. 2, pp. 69–71.

Ammonia Condenser, The. By A. G. Solomon. *Practical Engineer*, Vol. 18, 1914, No. 6, pp. 355–359.

Ammonia, Electrochemical, Oxidation of. By G. Oesterheld. *Zeitschrift fuer anorganische Chemie*, Vol. 86, 1914, No. 2, pp. 105–142.

Ammonia, Synthetic, by the Serpek Process. By Herre. *Chemiker Zeitung*, Vol. 38, 1914, No. 29, pp. 317–318.

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MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF APRIL, 1914

ORGANIC CHEMICALS

Item	Unit	Low		High
Acetanilid	Lb.	21½	@	22
Acetic Acid (28 per cent)	C.	1.50	@	1.65
Acetone (drums)	Lb.	10½	@	11
Alcohol, denatured (180 proof)	Gal.	35	@	37
Alcohol, grain (188 proof)	Gal.	2.52	@	2.54
Alcohol, wood (95 per cent)	Gal.	45	@	47
Amyl Acetate	Gal.	1.60	@	1.65
Aniline Oil	Lb.	9½	@	10
Benzoic Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal	23	to	25
Camphor (refined in bulk)	Lb.	—	@	42½
Carbolic Acid (drums)	Lb.	7¾	@	10
Carbon Bisulfide	Lb.	6¼	@	8
Carbon Tetrachloride (drums)	Lb.	7¼	@	7½
Chloroform	Lb.	19	@	24
Citric Acid (domestic), crystals	Lb.	51	@	51½
Dextrine (corn)	C.	2.52	@	2.72
Dextrine (imported potato)	Lb.	5½	@	6½
Ether (U. S. P., 1900)	Lb.	18	@	24
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19½	@	19¾
Oxalic Acid	Lb.	7¼	@	7½
Pyrogallic Acid (bulk)	Lb.	1.20	@	1.40
Salicylic Acid	Lb.	25	@	27
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	1.84	@	2.50
Starch (potato)	Lb.	5	@	5½
Starch (rice)	Lb.	7	@	8
Starch (sago)	Lb.	2⅜	@	2¾
Starch (wheat)	Lb.	5¼	@	6½
Tannic Acid (commercial)	Lb.	35	—	36
Tartaric Acid, crystals	Lb.	—	@	30¼

INORGANIC CHEMICALS

Item	Unit	Low		High
Acetate of Lead (brown, broken)	Lb.	7¼	@	7½
Acetate of Lime (gray)	C.	1.50	@	1.55
Alum (lump)	C.	1.75	@	2.00
Aluminum Sulfate (high-grade)	C.	1.25	@	1.75
Ammonium Carbonate, domestic	Lb.	8	@	8½
Ammonium Chloride, gray	Lb.	5⅞	@	6⅛
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3	@	3¼
Barium Chloride	C.	1.60	@	1.62½
Barium Nitrate	Lb.	5	to	5¼
Barytes (prime white, foreign)	Ton	19.00	@	23.50
Bleaching Powder (35 per cent)	C.	1.20	@	1.30
Blue Vitriol	C.	4.80	@	5.00
Borax, crystals (bags)	Lb.	3¾	@	4½
Boric Acid, crystals (powd.)	Lb.	7	@	8
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	57½	@	65
Chalk (light precipitated)	Lb.	4	@	4½
China Clay (imported)	Ton	nominal		
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign	Ton	16.00	@	17.00
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.65
Iodine (resublimed)	Lb.	3.55	@	3.60
Lead Nitrate	Lb.	8	@	8⅛
Litharge (American)	Lb.	5½	@	5¾
Lithium Carbonate	Lb.	65	@	70
Magnesium Carbonate	Lb.	21	@	35
Magnesite "Calcined"	Ton	28.50	@	29.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphoric Acid (sp. gr. 1.75)	Lb.	20	@	24
Phosphorus	Lb.	45	@	1.00
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°	Lb.	6¾	@	7
Potassium Bromide	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%	C.	3⅛	@	3¼
Potassium Chlorate, crystals	Lb.	7¼	@	7¾
Potassium Cyanide (bulk), 98–99%	Lb.	19	@	22
Potassium Hydroxide	C.	3.87½	@	4.37½
Potassium Iodide (bulk)	Lb.	2.95	@	3.00
Potassium Nitrate (crude)	Lb.	4¾	@	5¼
Potassium Permanganate (bulk)	Lb.	9¾	@	10
Quicksilver, Flask (75 lbs.)		37.50	@	—
Red Lead (American)	Lb.	6	@	6¼
Salt Cake (glass-makers')	C.	55	@	65

Item	Unit	Low		High
Silver Nitrate	Oz.	36⅞	@	38⅞
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash (48 per cent)	C.	67½	@	72½
Sodium Acetate	Lb.	3¾	@	4⅛
Sodium Bicarbonate (domestic)	C.	1.00	@	1.10
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	4⅛	@	4⅞
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	7¼	@	7½
Sodium Hydroxide, 60 per cent	C.	1.55	@	1.57½
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot	C.	—	@	2.25
Sodium Silicate (liquid)		65	@	1.50
Strontium Nitrate	Lb.	6¾	@	7
Sulfur, Flowers (sublimed)	C.	2.20	@	2.60
Sulfur, Roll	C.	1.85	@	2.15
Sulfuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	11¼	@	12½
Tin Oxide	Lb.	42	@	44
White Lead (American, dry)	Lb.	5¼	@	5½
Zinc Carbonate	Lb.	8½	@	9
Zinc Chloride (granulated)	Lb.	4½	@	5
Zinc Oxide (American process)	Lb.	5¾	@	6¾
Zinc Sulfate	Lb.	2⅜	@	2⅝

OILS, WAXES, ETC.

Item	Unit	Low		High
Beeswax (pure white)	Lb.	45	@	47
Black Mineral Oil, 29 gravity	Gal.	13½	@	14
Castor Oil (No. 3)	Lb.	8¼	@	8½
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	6.45	@	6.50
Cottonseed Oil (crude), f. o. b. mill	Gal.	47	@	47½
Cottonseed Oil (p. s. y.)	Lb.	7⅜	@	7⅝
Cylinder Oil (light, filtered)	Gal	21½	@	32
Japan Wax	Lb	12½	@	13
Lard Oil (prime winter)	Gal.	93	@	95
Linseed Oil (raw)	Gal.	50	@	51
Menhaden Oil (crude)	Gal	nominal		
Neatsfoot Oil (20°)	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.)	Lb.	3⅛	@	3¼
Paraffine Oil (high viscosity)	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.)	Bbl.	4.35	@	—
Rosin Oil (first run)	Gal.	—	@	27
Shellac, T. N.	Lb.	16	@	16½
Spermaceti (cake)	Lb.	30	@	31
Sperm Oil (bleached winter), 38°	Gal.	72	@	73
Spindle Oil, No. 200	Gal.	17½	@	18½
Stearic Acid (double-pressed)	Lb.	8¾	@	11¼
Tallow (acidless)	Gal.	65	@	66
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	47	@	47¼

METALS

Item	Unit	Low		High
Aluminum (No. 1 ingots)	Lb.	17¾	@	18¼
Antimony (Hallet's)	Lb.	7	@	7¼
Bismuth (New York)	Lb.	2.05	@	2.10
Bronze powder	Lb.	50	@	3.00
Copper (electrolytic)	C.	14.30	@	14.37½
Copper (lake)	Lb.	14⅝	@	14⅞
Lead, N. Y.	Lb.	3.80	@	—
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	43.50	@	44.50
Silver	Oz.	58	@	58¼
Tin	C.	36.00	@	37.00
Zinc	C.	5.20	@	—

FERTILIZER MATERIALS

Item	Unit	Low		High
Ammonium Sulfate	C.	2.75	@	2.80
Blood, dried	Unit	—	@	3.45
Bone, 4½ and 50, ground, raw	Ton	29.00	@	30.00
Calcium Nitrate (Norwegian)	C.	2.05	@	2.15
Castor meal	Unit	nominal		
Fish Scrap, domestic, dried	Unit	nominal		
Phosphate, acid, 16 per cent bulk	Ton	7.00	@	—
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	2.25	@	2.50
Tennessee, 70–80 per cent	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent	Ton	39.07	@	—
Pyrites, furnace size, imported	Unit	0.13¼		
Tankage, high-grade	Unit	3.20	&	10