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Cash Register Research

AN EDITORIAL in a recent issue of the *Evening Bulletin* of Philadelphia on "Industrial Research in America" reflects the justifiable pride which we all share in the support of industrial research. The National Industrial Conference Board has computed that the annual expenditures for industrial research in the laboratories of the United States aggregate $200,000,000. More than a thousand of these research laboratories are in the various units of industry and to their expenditures are added the appropriations for various federal bureaus. Within seven years the number of firms having special research departments is said to have virtually doubled, and the point is properly made that in these laboratories is to be found one of the reasons for the industrial supremacy of the United States. American manufacturers have always been ready to replace old machinery with more efficient types, no matter how short the service of the discarded equipment, and now they are equally willing to adopt new processes, most of which are evolved by the industries, instead of waiting for discoveries to come from the laboratories in the institutions of higher learning.

INDUSTRIAL AND ENGINEERING CHEMISTRY has always occupied a place in the front ranks of those who have urged research in applied science, and has recorded with pleasure and pride the results of such investigations. In emphasizing applied science, the necessity of furthering fundamental research has never been overlooked. We have merely recognized that the majority of people are interested first in the results expressed in tangible things which they can use, see, and enjoy in a variety of ways. It is only when an obstacle is met which cannot be overcome until the sum of our knowledge is increased through the establishment of new truth that the necessity of accumulating knowledge for its own sake is borne in upon the majority of those who must pay the research bills. There are fortunately a considerable number of notable exceptions, but we realize that for far too many research to be attractive must be of the cash register variety. Every time a dollar is rung up for the support of research, they want the bell to summon some one with a basket to catch the returning dollars.

We believe that a careful study of the reasons why announcements of important advances in the chemical and other industries emanate more often from countries other than our own will disclose that our appreciation of the part fundamental science plays in industry is further from being adequately developed.

Industrial research, which has demonstrated that it is a profitable investment, receives support in increasing measure, notwithstanding the occasional setback at the hands of an isolated industry, or in one or two extreme cases from a trade association, because those who have come into temporary power believe only in cash register research. This support shows clearly that, industrially speaking, we have made gratifying progress in the first stage of our scientific development. We have still before us the very considerable undertaking of bringing our industrial leaders and our financial giants to understand that underlying all the benefits of applied science there is a foundation laid through research in fundamentals, all of which involves patience in the extreme, financial support in abundance, and the recruiting and training of our best brains.

The outlook is by no means discouraging. You can name a dozen industries, more foresighted than the others, which have long supported fundamental work in their own laboratories as well as in our universities. It is only when support is sought for basic research and particularly for the tools of research, both fundamental and applied, that this necessity of beginning at once the education of those who profit first and most directly from the results is impressed upon us.

We must continue our work of bringing the public to sympathetic appreciation of the relationships between science and our present level of civilization. There are still thousands of industrialists and financiers who do not understand the necessity of forming an alliance with applied science if they are to meet the demand for ever better materials of commerce. The exceptions, among even our leaders who recognize how vital is research in fundamentals and a supply of adequate tools for its furtherance, are so few as to lay a monumental task before us. This education, which must be carried forward primarily by scientific men themselves, will be slow of growth and at times discouraging in its returns, but we believe it is one of the most important activities in which we can at present engage.

The Farmer's Dollar

INTEREST which has been centered around the farmer's problem has led to a number of impartial investigations into his economic status, and one such inquiry under the auspices of the National Industrial Conference Board provides the best analysis of the expenditure of the total cash income of the average farmer that has so far been provided. Food accounts for 16.4 per cent, clothing 14.3, farm equipment 15.4, hired labor 12.3, rent 10.7, fuel and light 1.0, interest 7.7, taxes 6.3, fertilizer 3.1, and unclassified, made up of a number of miscellaneous items including whatever profit and saving he may be able to make, 12.8. From this unclassified item he must educate his children, make his contribution to religious activities, provide such culture as his home enjoys, and so on throughout the list not specifically indicated by the other items.

At the moment we are most impressed by the relation between his tax bill, his fertilizer bill, and the activities of his political friends who would save him from economic disaster. Taxes require 6.3 and fertilizer 3.1 per cent of his total cash income. It will be noted that the taxes, largely imposed by politicians, are twice the sum that the farmer pays for fertilizer. A group composed of certain representatives in Congress and gentlemen who pose as the farmers' duly appointed representatives but who, we believe, continually misrepresent their actual interests, would have the country go into business and at least subsidize fertilizer manufacture and distribution for the purpose of somewhat lowering this 3.1 per cent item. How much it could be reduced depends upon the imagination of the spokesman of the moment, and figures as high as 43 per cent have been mentioned in political addresses. In discussing the economics of the fertilizer problem, most of these orators are quite beyond their natural field of knowledge or activity.

Why not have the politicians devote attention to taxes, a professional question with them, where something might be done to affect more directly the economic status of the farmer? The fertilizer question is safer in the hands of experienced industry, governed by supply and demand and benefited by constantly advancing science.

A Unique Foundation

THE Ohio Chamber of Commerce at Columbus has created the Fuel-Power-Transportation Educational Foundation for the purpose of acquainting the public, through the schools and other agencies, with the fundamentals of the problems of fuel, power, and transportation. The Foundation undertakes to secure impartial facts on various phases of the topics named and to distribute these nationwide where they can be studied and evaluated and conclusions drawn by the individual. So far a Primer on Economics and a Study of St. Lawrence Waterway Project have appeared. At an early date a monograph on Fundamentals of Transportation Problem may be expected. Early in December there will be available for distribution a sixteen-page treatise on the Fundamentals of the Fertilizer Problem, in which a connection will be shown between our fuel, power, and fertilizer problems, besides setting forth in concise form important data applicable to the Muscle Shoals controversy. The booklet will contain no argument but will present facts as the investigator for the Foundation has uncovered them, and there is reason to expect that the information will be presented attractively to the student, the teacher, and the general public.

The work so far conducted by this unique Foundation has been warmly commended by educators and public men throughout the country, and a demand for the printed studies has clearly emphasized the need for the type of work which has been inaugurated by the Ohio Chamber of Commerce.

Government Purchases

UNTIL recently a duly signed government requisition has been acceptable as equivalent to cash in the bank, but the Comptroller-General of the United States has lately refused to pay bills for reprints, even though they were ordered on the proper government requisition. In the Comptroller-General's letter on the subject it is stated, among other things, that "this office may settle claims only in accordance with law, and that all persons having transactions with government agents are chargeable with knowledge of their limited authority." While the ruling will force the SOCIETY to take a stand which may make it inconvenient for government bureaus to purchase reprints, this is a small matter compared with the general effect upon business of such a ruling. Apparently, any firm accepting an order on a government requisition must hereafter establish all the legal aspects and the attitude which the Comptroller-General may assume toward the transaction before it is safe in delivering the goods ordered.

We still have difficulty in understanding why a duly signed and issued government requisition should be open to suspicion.

International Congresses

AMONG the many things of value lost through the World War was that informal yet efficient organization known as the International Congress of Applied Chemistry, which was responsible for holding once in three years a scientific conclave, truly international in its attendance, work, and publications. Four languages were official—French, Italian, German, and English. Representatives on an equal footing came from everywhere and were welcome. Latest accounts of scientific progress furnished the keynote.

How well we remember the last of these international congresses in 1912! There was the gathering in Washington in Continental Hall where the leader of each national delegation spoke following the playing of his national anthem by the Marine Band. There was a notable afternoon with the President of the United States, the reception, the half-day of sight-seeing, and then the special trains to New York where the work of the Congress was conducted.

Columbia University and the College of the City of New York fairly swarmed with hundreds of chemists. The meetings, held on the sectional plan according to subject, were open to all and at stated times the Congress gathered to hear the principal addresses delivered by representatives of the leading foreign countries. Here we heard the glowing account of the development of the arc process in Norway by Eyde himself. Bernthsen demonstrated that nitrogen and hydrogen could be compelled to combine to form ammonia. Perkin discoursed on synthetic rubber, and the address of Ciamician on photochemistry remains a classic. No one who saw the multitude of products of industrial chemistry which Duisberg brought from Germany will ever forget that occasion in the great hall at City College. Of course there were banquets, sight-seeing, garden parties, and receptions, but they were incidental. The Congress did real work, as the twenty-nine volumes now on our shelves amply testify.

The International Congress was able to function without a continuous organization and without a paid secretariat and headquarters subject to national influences. The Congress decided where its next meeting would be held, selected the man to be responsible at that place, and left it to him to form his own organization, work out the details, and proceed. The war spoiled the congress planned for 1915, which was to have been in Russia under the chairmanship of Doctor Walden, the eminent scientist who is the visiting lecturer at Cornell this semester.

It is history that the war gave rise to scientific organizations in several countries, and it is but natural that these should have been the ones to form a new international organization. With the effect of the war still upon them, conditions were at first imposed which prevented the adherence of the former enemy countries to the new union, but fortunately those difficulties have been remedied and any country, the science of which can be represented through a central national body, is welcome.

At first the principal business of the International Union of Pure and Applied Chemistry, which is sponsored by the International Research Council, was the creation of good will and better understandings and beginning anew the promotion of scientific work on a true international basis. Although some committees for scientific work have been formed, it is patent that the Union has added little, if anything, to the sum total of scientific knowledge and has devoted itself more to questions of policy and diplomacy through social activities. This has been going on for eight years, but for the last year or two the active members of the Union have come to realize that if it is to survive and perform a useful function its program must be changed.

The Union is too much restricted in membership and in the number of individuals involved to accomplish its own ends. At present it brings together far too few really to hasten the day of better international relationships. If augmented in numbers it meets too often, and at the basis of it all is the neglect of its real opportunity again to make available the advantages of the world international congress. It is conceivable that some of the work of the Union would require the meeting of a small group more frequently than once in three years, provided the Union can be looked upon as a sort of nucleus or holding organization to which is entrusted the promotion of chemistry, international so far as the science is concerned. This involves assuming responsibility for a scientific congress to be held very much along the lines of the old International Congress.

This subject from time to time has been forcefully brought to the attention of the officials of the Union and was discussed at the Washington meeting when Ernst Cohen, the president, stressed the importance of organizing a truly international congress of chemistry along democratic lines. At the recent meeting in Warsaw articles providing for such congresses were presented and incorporated into new statutes of the Union. These articles were passed unanimously, but according to the Union's rules must be held over until the next meeting, scheduled to take place in Holland in July, 1928. In order to avoid undue delay a committee has been set up charged with the formulation of detailed plans for such international congresses. It is expected, therefore, that with the adoption of the new statutes the Union will be in position to act upon the report of the committee. It seems unfortunate that there should be even a year's delay for many are becoming impatient, and it is already fifteen years since the chemists of the world have gathered together in a congress organized along democratic lines and devoted to science.

We hope that the International Union of Pure and Applied Chemistry will take leadership in this matter and make the most of its opportunities. It would be unfortunate should it be found necessary to set up any other organization.

Significant Trends in Nitrogen Fixation

A SYNTHETIC ammonia plant is under construction in Norway, contracts have been signed for similar work in Czechoslovakia, and preliminary arrangements are concluded for another in Poland, all under the direction of American chemical engineers. The indication is clear that the position of America in this field is at least very favorable. A belated start in the fixation of atmospheric nitrogen seems to have been overcome by the development of our own processes—so satisfactory as to more than hold their own in world competition.

The recently announced German-Norwegian nitrogen agreement between the Norsk Hydro and the I. G. Farbenindustrie is of real significance, especially at this time when nitrogen problems remain political issues with us. Commercial Attaché H. Sorensen at Oslo states that the famous plants at Notodden and Rjukan are to be completely modernized and the present annual production of 33,000 tons greatly increased. The Birkeland-Eyde arc process is to be replaced by the Haber-Bosch method. This change is based entirely upon economics for from three to four times as great a volume of nitrogen can be fixed per unit of power consumed by the synthetic ammonia process as is possible by the arc process, highly refined though it is by the genius of the Birkeland-Edye group.

Is it not significant that some other process was not chosen? And does this circumstance not offer additional proof of world trends in nitrogen fixation solely toward synthetic ammonia?

Not Good if Detached

YOU have frequently noted on your railway ticket a coupon marked "not good if detached," and a lecturer has used the phrase as the subject of an address in which he emphasizes the value of close attachment to high ideals, constructive work, and service. The phrase is equally applicable in describing the professional man who endeavors to pursue his work unconnected with the organization which represents his field of activity. It would be no more accurate to say that all good chemists belong to the AMERICAN CHEMICAL SOCIETY than that all members of the AMERICAN CHEMICAL SOCIETY are good chemists. But we maintain that these unattached chemists, these non-members of the SOCIETY, however good in their daily work, would be better chemists if attached. Better because the support of their professional society indicates an attitude of mind which is always to be found in the well-rounded professional man; better because it indicates a desire to have a part in the advancement of the science and to do what they can to assist their professional body in reaching the ideal in service to the race, the nation, the professional group, and the individual. "Not good if detached." Think it over.

A New Start in Industry

REQUESTS which occasionally come to us for men with industrial experience who would like to return to academic life, as senior research fellows or in some other equally dignified capacity, suggest that through the university a well-trained man may find his best opportunity for making a fresh start in industrial work. The difficulty of locating the exact niche into which a research man fits most comfortably is of course well known. Too often failure to find agreeable employment merely leads to increasing discomfort, with the individual transferred from place to place within the same organization in an effort to locate a position which he can fill with utmost advantage to his employer and himself.

In such instances we believe the scientist would do well to consider a return to academic halls. Here certain weaknesses in his training, discovered through contact with industry, might be strengthened while new contacts were being made, a further record being built up with new problems, and a fresh inspiration received for another embarkation upon industrial work.

As additional fellowships are established in our schools and coöperating arrangements are developed with government bureaus, such opportunities increase. We recommend consideration of this suggestion by those who feel that along another road lies their best chance for success.

Martha and Mary in Science

IN A recent issue we referred to the guessers and the accumulators as classified by W. D. Bancroft, and wish now to add to that comment a quotation from a lecture by A. V. Hill, of University College, London, who is at present non-resident lecturer at Cornell University.

"Martha represents the scientist always busy in his laboratory, collecting invaluable data. Mary takes the broad view, reflects and discusses, and listens to discussion. Science needs them both."

Surface Tension of Metals with Reference to Soldering Conditions[1]

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The drop-weight method has been adapted to the determination of the surface tensions of mercury at 25° C., lead and tin and alloys of lead and tin at 350° C. *in vacuo*, as well as the surface tension values for some alloys, common to soldering practices in dry hydrogen chloride at 350° C. In addition, some simple spreading tests have been carried out which, together with the surface-tension values, made possible the establishment of a theory for the mechanism of solder spreading.

As early as 1868 Quincke[2] made investigations on the surface tension of molten metals. Since then a large number of researches have been carried out, most of which have had little value owing to the inaccuracies of the methods. Thus far the best results have been obtained by Hogness,[3] who has evaluated the surface tensions of bismuth, lead, tin, cadmium, mercury, and zinc at various temperatures.

Most attempts to determine the reasons for non-soldering have resulted in the claim that oxide films on the metal to be soldered have caused the trouble and that the purpose of a flux was to remove the oxide film. Others have found fault with the purity of the solder. Only recently has it been suggested that changes in the surface tension of the molten solder might explain the spreading or non-spreading of the molten metal on the solid one.

Perhaps the most clearly stated suggestion of this type comes from Ladon,[4] who says that each metal requires different fluxes to obtain the best results; likewise flat and round work requires different fluxes and solders. The fact that the same flux does not work to advantage on all types of surfaces of even the same metal means that there is some condition present which is different than commonly thought. To solder, surfaces must be clean. Clean surfaces rapidly oxidize to give an oxide film. The present theory is that fluxes dissolve the film, allowing the molten solder to alloy with the metal. He states further that slowly oxidizing metals, such as copper or brass, scratched and cleaned in nitrogen cannot be well soldered, even in a non-oxidizing atmosphere, without a flux. A drop of molten solder placed on a clean metal remains in spherical form, but when a flux is placed on top it spreads out, indicating that the surface tension has been decreased. Ladon further points out that there may be other means of decreasing surface tension and that there is a possibility of getting around the use of fluxes.

With Ladon's statements in view, it becomes the object of this investigation to determine the surface tensions of the molten alloys of lead and tin, especially those used in the most common low-melting solders, and then to determine what effect, if any, fluxes have on the surface tension of these alloys.

Apparatus

The apparatus was an adaptation of that used in the drop-weight method (Figure 1). For producing a vacuum, a Cenco Hy-Vac pump backed up a mercury-vapor pump. The pumps were connected with a vacuum line in which was set a McLeod gage and stopcocks 1, 2, 3, and 4. At 5 a Pyrex bulb was sealed in the line and around it was placed a small wire-wound resistance furnace, 8, controlled by a lamp bank connected to the 110-volt line.

The furnace, 6, was of the wire resistor type wound on a Pyrex glass tube and mounted in a manner to facilitate its being moved in a vertical direction. The furnace was so constructed that it was possible to look through a window and watch the contents. A lamp and the mirror, 7, were arranged to assist in this.

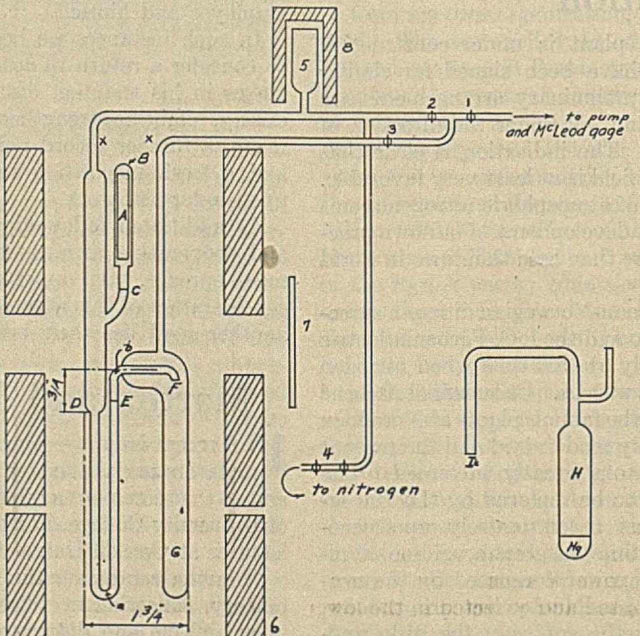

Figure 1—Diagram of Apparatus

Many difficulties were encountered in the development of the apparatus in which the drops were formed. Many different designs were tried before a satisfactory device was obtained. Figure 1 shows the tip for drop formation at *F*. This tip was made of Pyrex capillary tubing, which was first filled with Woods metal and then ground carefully by hand on a brass block using triple "f" carborundum powder as an abrasive, water being the lubricant. After grinding, the tip was mounted on the stage of a microscope and the orifice photographed at a known magnification. The picture of the orifice thus taken was measured carefully on a large number of diameters and the average of these values taken to be the effective diameter of the tip. The tip thus produced was sealed to a very fine capillary tube *a* (bore 0.2 mm.) at *E* and the whole capillary was then sealed into the section *G* by means of the ring seal at *b*. An extension, of 8- to 10-mm. tubing, was then sealed on at *D* with a side arm, *C*, to which was connected a larger piece of tubing, *B*, to hold the slug of solid metal, *A*. When us-

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[1] Received June 13, 1927. Presented before the Division of Industrial and Engineering Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *Pogg. Ann.*, **135**, 642 (1868).

[3] *J. Am. Chem. Soc.*, **43**, 1621 (1921).

[4] *Chem. Met. Eng.*, **24**, 981 (1921).

ing mercury the still, *H*, was sealed on instead of *B*. Great care had to be used in grinding the tips, as slight irregularities in the circumference of the orifice made large variations in the surface-tension values.

The method of surface-tension determination used was an adaptation of the drop-weight method outlined by Harkins and Humphrey.[5] By this method the weight of a drop of any liquid under consideration, forming under a given set of conditions, is determined, and by means of the density of the liquid and the radius of the tip on which the drop forms the surface tension is calculated by the formula

$$\alpha = \frac{Mg}{2\pi r\, f\left(\frac{r}{V^{1/3}}\right)}$$

α = dynes per cm.
M = weight in grams per drop
r = radius of tip, cms.
V = volume of drop
g = 980 dynes

Tips of varying size were used in determining the surface tension of mercury. The values for mercury obtained in each case were plotted against the diameter of the tip, as shown in Figure 2. The two most acceptable values for mercury are those determined by Ewing[6] and Hogness.[3] These, therefore, represented the maximum limits of variation and were considered as high and low values for the surface tension of mercury. The maximum sized tip allowable would give the minimum value, or that given by Hogness, while the minimum sized tip would give the value determined by Ewing. Therefore, tips having a diameter of between 0.11 and 0.14 cm. were used to obtain acceptable values for surface tension. This relationship proved to hold good for other metals besides mercury. A plot of these standardization values is given in Figure 2.

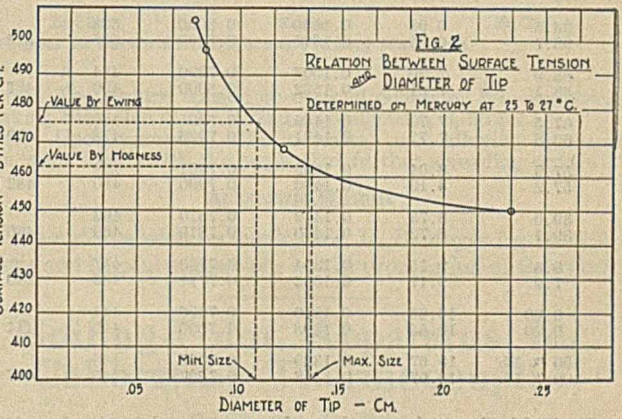
A slight modification of the general set-up shown in Figure 1 was made in the last part of the investigation to facilitate the admission of hydrochloric acid gas. Two stopcocks in series similar to those shown at 4 were placed in the vacuum line between *b* and *x*, so that a gas could be introduced into the system directly.

Some simple spreading tests were made using a common solder of 40 per cent tin–60 per cent lead and copper plate. For these tests a transparent furnace 16 inches (40 cm.) long was used. This furnace was made by winding about 20 inches (50 cm.) of No. 28 resistance wire on a Pyrex glass tube of 1$^1/_4$ inch (3 cm.) diameter. This tube was then mounted in another similar glass tube of 2-inch diameter so that a dead air space surrounded the first tube. The two together were in turn mounted in a third Pyrex tube, so that a second air space was available for insulating the furnace.

Manipulation

Mercury—The apparatus was disconnected from the system at *xx* and thoroughly cleaned and dried. The mercury still, *H*, was then sealed on and the whole apparatus connected at *xx* again. The furnace was removed and the system evacuated for 3 hours. At the end of this time the mercury was distilled into the dropping apparatus and, after cooling to room temperature, small increments of nitrogen were admitted by the manipulation of stopcocks. This procedure was continued until the column of mercury had been forced through *a* and into the horizontal portion of the tip *F*. The furnace around 5 was then turned on, the heat being increased very slowly so that the gas in the bulb was expanded, forcing the mercury out of the tip at the rate of about 1 drop every 5 seconds. The drops were counted and collected in the lower arm of the apparatus, where they were sealed off and later transferred to a weighing bottle to be weighed.

Lead and Tin—The procedure for lead and tin and their alloys was slightly different. *B* instead of *H* was sealed on at *c* and small slugs of the metal whose surface tension was to be determined were inserted in *B*. After the apparatus was sealed on at *xx* again, the system was evacuated until no pressure could be detected with the McLeod gage. The furnace 6 was then adjusted around the apparatus, the top and bottom being plugged with asbestos packing. A copper-constantan thermocouple (not shown in the diagram) was fastened to the glass at *D*. The apparatus was next heated to 425° C., causing the metal slug to melt and run down into *D*. Pumping was continued for from 5 to 6 hours, after which the temperature was dropped to 350° C. Oxygen-free nitrogen was admitted until drops were forced from the tip at the rate of about one drop per second. After twenty or thirty drops had been collected the entire system was filled with nitrogen and the sample was sealed off. Excess metal was then blown out of the reservoir, in order to save the apparatus for further determinations.



Spreading Tests—Spreading tests were carried out on cleaned and polished copper strips. Equal-sized samples of 40 per cent tin–60 per cent lead solder were laid on the strips, which were then sealed in a horizontal glass tube and evacuated. After evacuation had been completed the transparent furnace described above was adjusted around the tube and brought to a temperature of 350° C. The total period of heating was 45 minutes in all cases. This procedure was followed with the variation of adding fluxes to the solder before sealing into the tube. A run was also made introducing hydrochloric acid gas when the solder had melted.

Alloys—The alloys used in this work were made from Bureau of Standards tin having a melting point of 231.9° C. and from Betts lead made by the electrolysis of lead silicofluoride. This lead and the tin were also used for the determination of the surface tension of the pure metals. All samples were melted in a small graphite crucible and cast in a warm iron mold. The alloys were carefully skimmed before casting and all had a very bright surface free from oxide after solidification. The mercury was purified by a double distillation before use, and was finally distilled into the apparatus.

The sample of alloy from which the weight of the drops was obtained was saved for analysis, being cut into very fine pieces with a hacksaw and the pieces thoroughly mixed before being analyzed.

Analysis for lead was made using the standard ammonium molybdate titration. The densities of the alloys and metals used in the calculations were those given by Apri,[7] while

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[5] *J. Am. Chem. Soc.*, **38**, 228 (1916).

[6] *Ibid.*, **42**, 2539 (1920).

[7] *Intern. Z. Metallog.*, **5**, 142 (1913–14).

the correction factors of $f\left(\frac{r}{V^{1/3}}\right)$ used were those given by Harkins and Humphrey.[8]

Discussion of Results

An average of seven determinations gives the value of 468 dynes per centimeter for mercury at 25° to 27° C. This average value falls between the values determined by Hogness and Ewing at the same temperature and the average deviation is 4 dynes. Hogness' value was 463, or about 1 per cent lower than 468, while Ewing's evaluation was 476, which is about 1.5 per cent higher. Such differences may easily be due to the differences in method and experimental error, since this adaptation of the drop-weight method is accurate to only 1.5 per cent.

Table I—Surface Tension at 350° C. of Lead and Tin and the Alloys of Lead and Tin *in Vacuo*

Tin	Density	Weight per Drop	$f\left(\frac{r}{V^{1/3}}\right)$	Surface Tension	
Per cent		*Gram*		*Dynes per cm.*	*Av.*
100	6.97	0.1642	0.8060	523	
100	6.97	0.1639	0.8060	521	
100	6.97	0.1664	0.8071	528	524
98.5	6.98	0.1630	0.8090	523	
98.7	6.98	0.1645	0.8090	525	524
88.9	7.20	0.1507	0.7990	484	
88.1	7.21	0.1532	0.8000	490	487
67.5	7.70	0.1489	0.7925	480	
68.8	7.72	0.1481	0.7925	478	479
57.9	8.04	0.1499	0.7901	484	
57.2	8.10	0.1480	0.7900	480	482
39.0	8.73	0.1419	0.7810	463	
39.1	8.73	0.1440	0.7810	469	466
8.5	9.15	0.1354	0.7730	447	
7.9	9.17	0.1302	0.7711	433	440
0.80	10.65	0.1310	0.7590	441	
0.70	10.65	0.1308	0.7590	440	441
100 % Pb	10.67	0.1329	0.7607	448	
100 % Pb	10.67	0.1318	0.7594	445	447

In Table I are shown the values obtained for lead and tin and for the alloys of lead and tin *in vacuo*. The surface tensions of lead and tin compare favorably with those of Hogness, as shown in the following tabulation:

	Hogness	Observed	Difference
	Dynes per cm.		*Per cent*
Lead	442	446	1.00
Tin	522	524	0.40

The values for lead and tin and for the alloys both *in vacuo* and in dry hydrochloric acid gas are plotted in Figure 3 against the percentage of tin. It is seen that the addition of lead to tin causes a very pronounced drop in the surface tension of tin, while small quantities of tin drop the surface tension of lead only slightly and then raise the value of the surface tension until the value for pure tin is reached.

This lowering of the surface tension of tin by lead seems to indicate that Smith[9] was correct in his statement that the larger the difference in atomic volumes and surface tensions between two metals the more of a decrease will be obtained in surface tension upon alloying the two. This leads one to believe that a conclusion might be made as to which elements would form the best solders from the standpoint of spreading—that is, those solders with the lowest surface tension.

The following table then indicates that, other things being equal, alloys of bismuth and lead, and antimony and lead, would have a lower surface tension than those of tin and lead, being better suited for soldering operations from the standpoint of surface tension. The surface tension of thalium would probably be very close to that of lead. If this should be true solders using thalium with antimony, bismuth, or tin ought to be superior to others, since there is a much greater difference in atomic volumes.

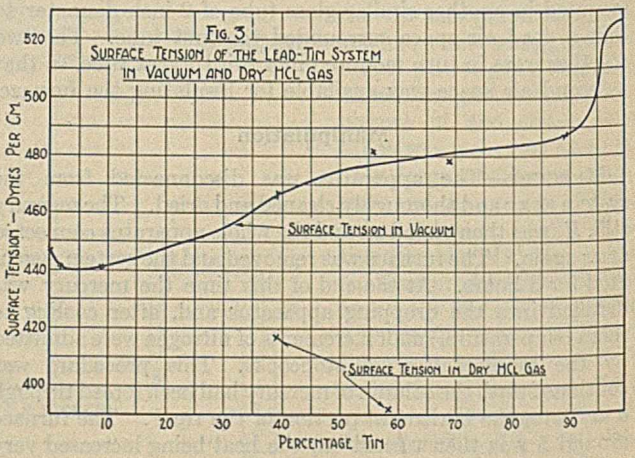
Element	Atomic Volume[10]	Surface Tension	Element	Atomic Volume[10]	Surface Tension
Al	10	520	Sn	12	524
Fe	12	1000	Sb	12	274 (?)
Cu	11	1175	Tl	48	...
Zn	9.7	758	Pb	29	446
Cd	17	630	Bi	13	269
Ag	23	855			

It has long been the concensus of opinion that hydrochloric acid is the active constituent in the better soldering fluxes. The ordinary flux used by tinners consists of zinc dissolved in an excess of hydrochloric acid. Another efficient flux is ammonium chloride, which is readily dissociated into ammonia and hydrochloric acid at soldering temperatures. Consequently, the interfacial tension between two solders and dry hydrochloric acid gas was determined. The two solders were 40 per cent tin–60 per cent lead and 60 per cent tin–40 per cent lead. Table II shows the results of these determinations compared with the surface tensions of the same alloys *in vacuo* and in nitrogen. The presence of dry hydrochloric acid gas lowers the surface tension of the 60–40 solder 18.8 per cent, while the lowering in the case of the 40–60 solder is 12 per cent. Nitrogen seems to raise the surface tension values very slightly.

Table II—Surface Tension at 350° C. of Two Solders *in Vacuo*, Dry Hydrochloric Acid Gas and Nitrogen

Tin	Density	Weight per Drop	$f\left(\frac{r}{V^{1/3}}\right)$	Surface Tension		Atmosphere
Per cent		*Gram*		*Dynes per cm.*	*Av.*	
57.9	8.04	0.1499	0.7900	484		
57.2	8.10	0.1480	0.7901	480	482	Vacuum
39.0	8.73	0.1419	0.7810	463		
39.1	8.73	0.1440	0.7810	469	466	Vacuum
57.5	8.07	0.1203	0.7740	397		
57.5	8.07	0.1161	0.7719	385	391	HCl gas
39.0	8.73	0.1235	0.7705	425		
39.0	8.73	0.1221	0.7695	407	416	HCl gas
57.5	8.07	0.1527	0.7890	496		
57.5	8.07	0.1530	0.7800	497	497	Nitrogen

This decrease in surface tension may possibly be explained by assuming that hydrochloric acid reacts with the lead and tin present to give the chlorides of the metals probably concentrated in the surface of the drops, thus changing the number and kind of the molecules present and consequently causing a variation in the forces of attraction in the metal.



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[8] *J. Am. Chem. Soc.*, **38**, 228 (1916).

[9] *J. Inst. Metals*, **12**, 168 (1914).

[10] *Science*, **61**, 554 (1925).

Feldman[11] has established a relationship for spreading represented by the following equation:

$$S = Wa - Wc$$

where S is the spreading coefficient, Wa is the work of adhesion, and Wc is the work of cohesion which is equal to the surface tension. Since the surface tension is decreased by hydrochloric acid, the value for S must be increased provided Wa is not decreased correspondingly, so that there is a greater tendency for spreading in the presence of a fluxing material.

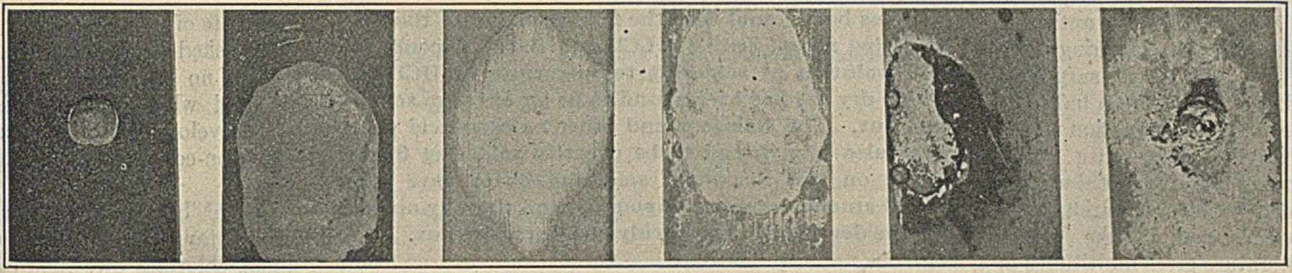
No flux NH$_4$Cl Dry HCl gas ZnCl$_2$ Rosin SnCl$_2$

Figure 4—Spreading Power of 40% Sn–60% Pb on Clean Copper *in Vacuo* with Different Fluxing Materials

To demonstrate further in a simple manner this effect of decrease in surface tension on the spreading of a solder, some spreading tests were carried out as previously described. The results shown in Figure 4 may be interpreted as follows:

1—The order of fluxing effect from the most efficient to the least efficient is from NH_4Cl to $SnCl_2$, although NH_4Cl, HCl, and $ZnCl_2$ are all very good.

2—Careful examination will reveal that around the outer edges of the spread portions there is an extended area where the solder has penetrated the solid copper. This shows actual alloying between the copper and solder, with a consequent increase in the work of adhesion, Wa.

3—Since hydrochloric acid gas decreases the surface tension of solder, it may be seen that these other fluxes likewise reduce the surface tension of the solder.

From these observations it may be said that the probable effect of fluxes in soldering operations is:

1—The surface tension or work of cohesion, Wc, decreases, making the value of S greater.

2—Upon an increase in S some spreading takes place with alloying, increasing Wa to some extent, and finally making the value of S still larger, with the result that further spreading occurs.

Conclusions and Summary

By means of the foregoing experiments several relationships have been established, which should be at least suggestive for further work on the problem of metal joining.

1—A new adaptation of the drop-weight method has been developed, which is capable of obtaining check results which are within 1.5 per cent of each other.

2—The surface tensions of mercury at 25° C., lead, and tin and their alloys at 350° C. have been determined *in vacuo*. The numerical results for all three metals compare favorably with those obtained by other investigators.

3—The addition of lead to tin materially decreases the surface tension of tin, while the addition of tin to lead decreases the surface tension of lead to only a very small extent and is followed, upon further addition of tin, by a rise in the surface tension.

4—It might be possible to obtain a solder of much lower surface tension than those now used by alloying metals with widely different surface tensions and atomic volumes. For example, thallium and bismuth or thallium and antimony might produce a good solder from the standpoint of spreading.

5—A very decided lowering of the surface tension is to be noted in the case of solders when determined in an atmosphere of dry hydrochloric acid gas.

6—There is a very slight rise of surface tension in solders when determined in an atmosphere of nitrogen.

7—The mechanism of the spreading of solder in soldering processes is pictured as taking place in two steps:

(*a*) The surface tension or work of cohesion, Wc, decreases, making the value of the spreading coefficient, S, larger.

(*b*) Upon spreading, Wa increases, since alloying increases the value for S, with the result that further spreading occurs.

Acknowledgment

The authors wish to thank Prof. D. B. Keyes for his criticisms and helpful suggestions in the prosecution of this work.

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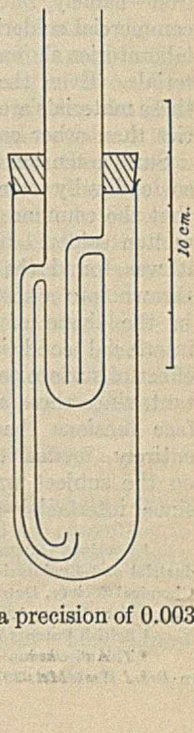
[11] *J. Am. Chem. Soc.*, **44**, 2665 (1922).

Boiling-Point Apparatus for Calibrating Thermocouples[1]

By Thomas De Vries

Purdue University, Lafayette, Ind.

In the usual procedure of calibrating thermocouples by suspending the thermocouple in the vapors above the boiling liquid and protected by a radiation shield, superheating of the vapors frequently occurs. To prevent this, a modified McCoy apparatus was designed in which the vapors must first bubble through some of the liquid before passing up and around the thermocouple, which, as usual, was enclosed in a glass tube and filled to 1 cm., and no more, with paraffin. The return tube must be bent upwards to prevent percolating action, and the end must be entirely covered with the liquid. A radiation shield is not necessary, since the walls of the inner tube, heated by the vapors from the outside, serve as an excellent shield.



With the end of an eight-junction copper-constantan thermocouple just above the boiling liquid (naphthalene) in the inner tube, and the condensation line about 4 cm. above the cork, the author was easily able to obtain temperatures constant to 1 microvolt, the limit of the potentiometer used. This corresponds to a precision of 0.003 degree.

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[1] Received October 15, 1927.

The Action of Fluxes in Soft Soldering and A New Class of Fluxes for Soft Soldering[1]

By R. S. Dean and R. V. Wilson

Manufacturing Development Branch, Western Electric Company, Inc., Chicago, Ill.

It has been found that the fluxing action of the best soldering fluxes, $ZnCl_2$, NH_4Cl, and $SnCl_2$, depends on the evolution at soldering temperatures of HCl gas, which dry gas has been found to be an effective soldering flux. The halogens and other halogen acid gases have also been found to be effective soldering fluxes. Based on this discovery, soldering fluxes have been found among organic compounds, and the way opened for the development of a truly non-corrosive flux.

DESPITE the antiquity of the soldering process, it is surprising that there has been but little scientific investigation of the "why" of soldering. The great mass of material written on the subject in various periodicals and in the patent literature gives multitudes of formulas for solders and fluxes varying from skunk oil[2] to the chlorides of the rarer elements.[3] From it all one can but conclude that, even though many mixtures have been suggested as a result of cut-and-try methods, little has really been done on the more fundamental aspects of the problem.

Present Accepted Theory of Soldering

The most commonly accepted theory of soldering has been that the function of a flux is to clean and keep clean the surface to be soldered either by removing the oxides and other impurities present by reaction with inorganic fluxes or by reducing or dissolving them with organic materials.[4] Such a theory is quite patent on the face of it, but unfortunately it does not explain why certain materials are so much better soldering fluxes than others of similar nature. It is also difficult to reconcile such a theory with the fact that of all the theoretically possible compounds only three have been found which facilitate to any marked degree the spread of a lead-tin or soft solder on copper, brass, or iron—namely, $ZnCl_2$, $SnCl_2$, and NH_4Cl. Every efficacious commercial soldering flux which has been analyzed in these laboratories shows the presence of one or more of these materials. Even the most casual observation will show that these materials are of quite a different order of fluxing properties than other constituents of commercial soldering fluxes.

Surface tension has been considered an important factor in solder flow by some investigators. Crow,[4] however, maintains that the common fluxes do not affect the surface tension of molten solder. In the course of the present investigation it was found that when zinc or ammonium chloride was thrown into a test tube of molten solder a decided change in the shape of the meniscus occurred. Whatever the interfacial condition might be, the authors felt that the effect of surface tension of the flux could not be very important, since there are other salts with as high or higher surface tensions than zinc or stannous chlorides which are entirely ineffective as soldering fluxes. Further study on the subject was not deemed worth while at this time, since interfacial relations are so complicated that, were the facts of the case definitely established one way or the other, no theory could be evolved which would aid in the development of a suitable non-corrosive soldering flux.

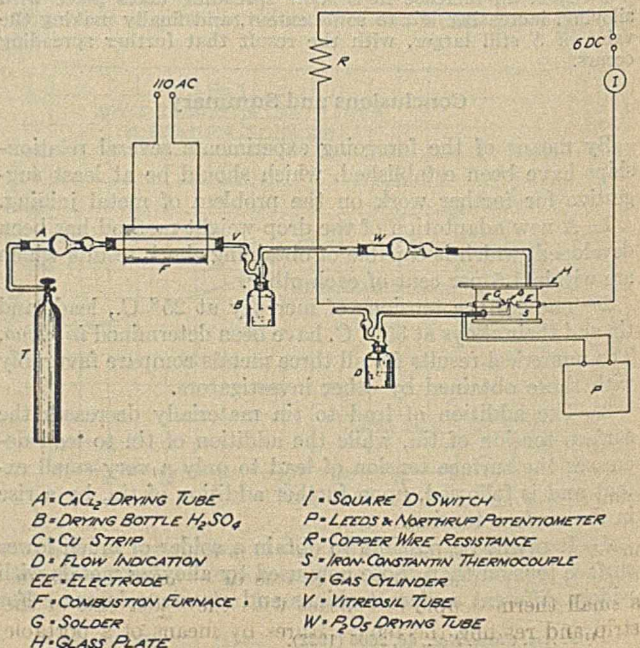
Dean[5] has suggested that zinc, stannous and ammonium chlorides owe their action to the evolution of hydrochloric acid gas, which displaces the air on the work and which is subsequently displaced in some manner by the solder.

Purpose and Method of Attack in Present Investigation

The present investigation was undertaken with the idea of setting up a quantitative evaluation of fluxing power in order to study the effect of various gases on the soldering process. By this means it was hoped that some light might be thrown on the mode of action of fluxes in general, and that the suggestion that the chloride fluxes owe their action to the evolution of gaseous hydrochloric acid might be critically tested.

Experimental

Any method of evaluating fluxing power must take into consideration the following factors: (1) uniformity of tem-



Apparatus for Testing Efficiency of Soldering Fluxes
Fig. 1

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[1] Received August 3, 1927. Presented before the Division of Industrial and Engineering Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] U. S. Patent 1,321,529 (November 11, 1919).

[3] British Patents 170,343 (July 10, 1920) and 217,880 (June 20, 1923).

[4] This discussion appeared in several British journals but is assembled in *Brass World*, **21**, 39 (1925).

[5] "Theoretical Metallurgy," p. 150, John Wiley & Sons, Inc., New York.

Table I

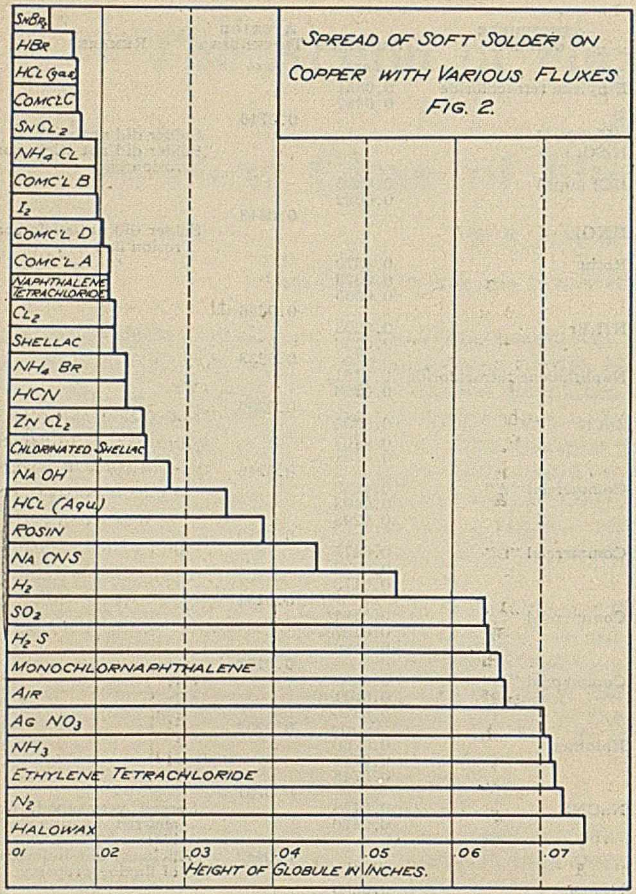
ATMOSPHERE OR FLUX	THICKNESS	AVERAGE THICKNESS	REMARKS
	Inch	*Inch*	
N_2	0.0645		
	0.0663		
	0.0842		
	0.0835		
	0.0643		
		0.0726	
H_2	0.0510		
	0.0480		
	0.0553		
	0.0610		
	0.0568		
	0.0497		
	0.0535		
	0.0552		
	0.0550		
		0.0539	
Air	0.0662		
	0.0678		
	0.0648		
		0.0663	
HCl (gas) (dry)	0.0165		Carefully dried over P_2O_5
	0.0180		
	0.0172		
		0.0172	
Cl_2	0.0233		
	0.0200		
		0.0216	
SO_2	0.0687		
	0.0590		Surface of copper bright
	0.0646		
		0.0641	
NH_3	0.0692		
	0.0709		Green to red film on copper
	0.0736		Corrosion slight
		0.0712	
H_2S	0.0643		Copper and solder thickly coated with black sulfide
		0.0643	
HCN	0.0232	0.0232	
HBr	0.0168	0.0168	Solder and copper badly corroded
Chlorinated shellac (alcohol solution)			Flux boils up and prevents solder from sticking
Shellac	0.0208		Shellac charred badly
	0.0218		
	0.0222		
		0.0216	
NaOH	0.0241		Copper and solder attacked
	0.0291		
	0.0310		
		0.0281	
Pyrogallic acid			Flux charred preventing adherence of solder to strip
Chlorinated shellac (solid)	0.0239		Shellac charred
	0.0246		
	0.0277		
		0.0254	
I_2	0.0195		Corrosion bad
	0.0198		
		0.0196	
Monochloronaphthalene	0.0683		
	0.0631		
		0.0657	
Ethylene tetrachloride	0.0851		
	0.0682		
		0.0716	
CH_3COOH			Solder did not stick
H_2SO_4			Solder did not stick, corrosion bad
HCl (aqu.)	0.0305		
	0.0382		
		0.0343	
HNO_3			Solder did not stick, corrosion bad
Rosin	0.0370		
	0.0393		
	0.0395		
		0.0386	
NH_4Br	0.0208		
	0.0258		
		0.0233	
Naphthalene tetrachloride	0.0191		
	0.0228		
		0.0209	
$ZnCl_2$	0.0255		
	0.0262		
	0.0231		
		0.0249	
Commercial "A"	0.0230		
	0.0193		
	0.0208		
		0.0210	
Commercial "B"	0.0175		
	0.0233		
	0.0173		
		0.0194	
Commercial "C"	0.0191		
	0.0137		
	0.0189		
		0.0172	
Commercial "D"	0.0200		
	0.0211		
	0.0195		
		0.0202	
Halowax	0.0760		
	0.0745		
	0.0748		
		0.0751	
NaCNS	0.0428		Spread very good, flux charred causing bubbles
	0.0470		
		0.0449	Thickness not indicative of fluxing property
NH_4Cl	0.0198		
	0.0191		
		0.0194	
Na_2SO_3			Globules did not adhere to copper
$AgNO_3$	0.0720		
	0.0688		
		0.0704	
$SnCl_2$	0.0195		
	0.0155		
		0.0175	
$SnBr_2$	0.0148		
	0.0130		
		0.0139	
KI			Solder globule did not stick to strip

perature and composition of the solder and metal, (2) time required to bring the solder and metal to the desired temperature, (3) time the flux is allowed to act, (4) uniformity of the surface on which the solder spreads. To keep these factors as nearly constant as possible and at the same time provide a convenient means of measuring the solder spread, the apparatus shown in Figure 1 was set up. The spread of the solder (55-45, Pb-Sn) could be determined by measuring the thickness of the globule with a micrometer, since uniform pieces of solder were used. Copper strips 0.375 inch wide and 0.0050 inch thick were used as supports for the solder. To insure a uniformly clean surface all the strips were polished with the finest grade of French emery paper, washed, and dried in alcohol immediately before using. Heating was accomplished by placing the strips firmly between the electrodes of the apparatus and passing a current of 185 amperes at 6 volts through the strips. Since the strips were of uniform size and the current constant, it was possible to obtain a constant speed of heating on all the samples. The current was allowed to flow only until the desired temperature was reached, which in the present experiments was 10 seconds. 200° C. was found to be a convenient temperature. The temperature was determined by placing a small thermocouple in contact with the under side of the strip and reading the temperatures by means of a portable Leeds and Northrup potentiometer. In practice the instrument was set at 200° C. and the current allowed to flow until the pointer on the galvanometer swung to zero. The atmosphere could, of course, be varied by placing the glass plate (sealed with vaseline) on the lapped surface of the apparatus and passing the desired gas through the openings provided. A bend in the strips was necessary to allow for the expansion of the copper as it was heated. In the case of powdered fluxes a small amount was sprinkled on the surface of the polished strip, the solder placed thereon, and the strip heated as described above. A drop of the liquids was sufficient to cover the surface of the strip and the solder was placed on the center as before. In the case of gases the strip and solder were put in place, the apparatus closed, and gas passed through until all the air had been displaced.

Experimental Results and Discussion

The thicknesses of a solder globule weighing 0.13 gram (± 2 per cent) for all of the substances tried are assembled in Table I. The thickness in all cases includes the copper strips, which were of uniform thickness.

Figure 2 is a graphic representation of the relative thickness of the globules of those substances tried which caused the solder to adhere to copper.



Spread of Soft Solder on Copper with Various Fluxes
Fig. 2.

These results show that dry gaseous hydrochloric acid[6] is among the best soldering fluxes, as are hydrobromic acid and chlorine. An examination of the other good soldering fluxes as disclosed by this work indicates that they are compounds which give off halogens or halogen-acid gases on heating. The only exceptions are shellac and hydrocyanic acid, which latter has many properties in common with the halogen acid. We are accordingly led to the very interesting conclusion that good soldering fluxes depend for their action on the evolution of a halogen or a halogen acid at soldering temperatures. Just how these halogens or halogen acids promote the flow of solder has not been determined in this investigation, but it is suggested that they act to displace the adsorbed air on the metal with a layer of gas, which subsequently is removed by reaction with the solder.

Note—The zinc and stannous chlorides used were the hydrated salts. It was found that drying zinc chloride over phosphorus pentoxide changed the soldering characteristics only in that the temperature necessary for fusion of the salt (and evolution of the hydrochloric acid) was considerably higher.

Outlook for a Truly Non-Corrosive Flux

From a consideration of the results it was possible to define clearly the requirements of a good soldering flux which would be truly non-corrosive and yet be as effective as the metallic chlorides now in use. Such a flux should be insoluble in water (incapable of hydrolysis), should at soldering temperatures (approximately 200° C.) liberate an acid gas and leave as reaction products no compounds which are themselves corrosive or a hindrance to solder flow. Such a compound might be expected to be found among the halogenated hydrocarbons, such as hexabromomethane and dibromoanthracene tetrabromide, of sufficiently high molecular weight to be insoluble in water. Naphthalene tetrachloride has been found quite satisfactory for certain types of commercial work and is now in use. This flux, however, gives off hydrochloric acid at low enough temperatures so that it is condensed by the moisture on the metal surrounding the soldered joint and a litmus paper test reveals a slight acid reaction. A number of other compounds of this type have been prepared which are fairly good fluxes but which offer the same difficulties. Among them are 9, 10-dichloroanthracene tetrachloride 1, 2, 3, 4, α, β, dichlorocinnamic acid, and naphthalene tetrabromide. The work along this line is being continued and it is thought that a compound giving chlorine rather than hydrogen chloride might be better since chlorine is not so hygroscopic.

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[6] Coffman and Parr, page 1308, this issue, have substantiated this conclusion that dry gaseous HCl is a good soldering flux.

Electrical Heating Equipment for Chemical Works[1]

By G. Angel[2]

Bohus, Sweden

IN CHEMICAL manufacturing practice difficulties are often encountered in evaporating or heating strong acids or other corrosive liquids. If a resistant material or coating for the vessel is found this is often a heat insulator, such as glass, fused quartz glass, stoneware, rubber, and bitumen. In these cases the equipment shown in Figure 1 has proved to be excellent where cheap electrical energy is available.

Inside Heating by Lighting Arcs

The figure shows an iron tank lined with acid-proof tiles, although any kind of vessel resistant to the action of the liquid may be used. In the center are placed two electrodes of graphite or other suitable material, surrounded by pipes of chemical stoneware or fused quartz glass. In their upper ends rough asbestos packings are placed.

After the current is turned on the pipes quickly become filled with vapor, so that the electrodes are in contact with the liquids only at their ends. Owing to the high current density at these points, lighting arcs begin to burn. Either direct or alternating current, one- or three-phase, can be employed. If direct current is used and the tank is of a conducting material only one central electrode is necessary, for the vessel itself can be used as the other. In that case it is advisable that the vessel be connected with the negative pole of the generator in order to diminish corrosion. This arrangement makes it possible to employ a cheaper non-resistant material for the vessel. A sufficiently high negative potential may be maintained, however, as long as the vessel contains liquid and this should be carefully washed out afterwards.

The energy consumption and heat evolution are easily regulated by moving the electrodes in the pipes forward or backward, thus increasing or decreasing the current strength. The voltage used in the writer's experiments has covered

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[1] Received July 5, 1927.

[2] Present address, Nybrogatan 77, Stockholm, Sweden.

a range of from 60 to 500 volts, although without doubt a considerably higher voltage may be used. The lighting-arc method makes possible the use of a higher tension than heating by electrodes not surrounded by a gas atmosphere.

Combination with Electrolysis

In some cases the heating process can advantageously be combined with electrolysis—e. g., to produce or prevent reduction or oxidation or to diminish the corrosion of the vessel as described above. The choice of electrode materials and current densities affords the means of regulating the oxidation potential. For instance, when oxidation is desired, a high anodic current density and an anode material with high overvoltage should be employed, while the current density of the cathode should be kept low by using the vessel as cathode. If necessary, a diaphragm can be used.

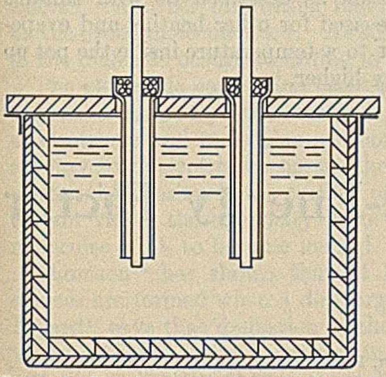


Figure 1—Heating Equipment for Liquids

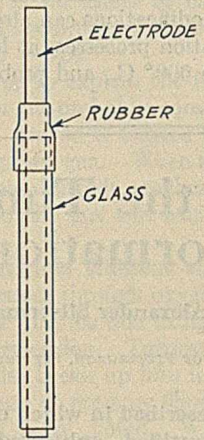


Figure 2—Electrode for Laboratory Research

Applications

This method has proved satisfactory for several practical purposes, its main advantages being the cheapness and simplicity of the construction and the high energy efficiency, which approaches 100 per cent.

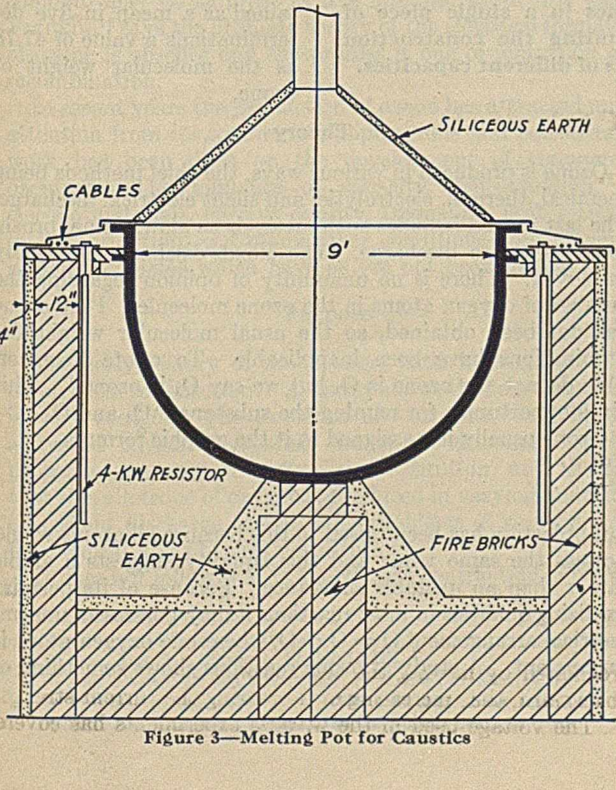


Figure 3—Melting Pot for Caustics

For heating concentrated hydrochloric acid electrodes of graphite were used, the pipes and vessel being of fused quartz glass.

For sodium sulfate and sodium chloride solutions iron was a sufficiently resistant material for electrodes and tanks.

Zinc chloride solution has been evaporated to a specific gravity of about 2.0 with a zinc rod as anode and the iron tank as cathode.

For laboratory research an electrode of the construction shown in Figure 2 has been used. A heating equipment placed in a pipe line prevented much trouble in one case where the pipes frequently got stopped up with potassium chlorate which crystallized out on cooling. It may be observed that the current is automatically shut off when the level of the liquid falls below the ends of the electrodes.

The method described above was worked out in conjunction with P. O. Björkman. It is not generally applicable where electrical heating or evaporation of solutions is to be performed, as when the solutions are non-conductors or when a local overheating is to be avoided. In some cases the disintegration of the electrodes and consequent contamination of the solution with electrode particles causes difficulties which cannot be surmounted. In such cases metallic resistors outside the vessel must be used if the heating is to be produced electrically.

Outside Heating by Resistors

Figure 3 shows an electrically heated pot for the finishing melting of caustics which the writer has tried on a large scale. The pot is about 9 feet in diameter and holds about 10 tons of caustic. Sixty electrically heated coils are placed around the pot, hanging down vertically. They are made of two parallel nichrome wires, 1.35 mm. in diameter, wound on pieces of fireproof china (Figure 4). Each of these pieces is only 4 inches high in order to diminish the risk of breaks. They are held together and supported by an iron rod passing through holes in the center and connected at the upper end with a wire from the neutral point of the transformer and at the lower end with the nichrome wires by means of 4.5-mm. monel wires. Each resistor has a capacity of 4 kilowatts, the maximum power consumption thus being 240 kilowatts when all resistors are connected; 220 volt a. c. is used.

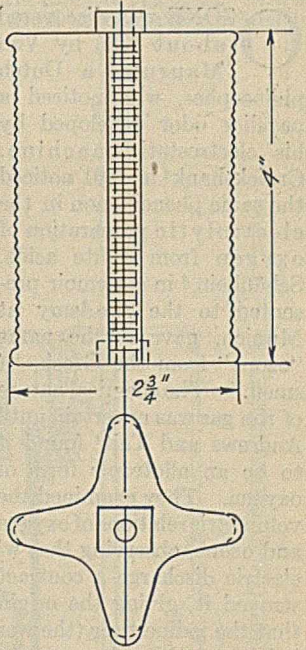


Figure 4—China-Ware Insulator

The walls and bottom of the furnace are made of fire brick, the upper part of magnesite. It is further insulated against heat losses by means of siliceous earth outside the walls and inside the bottom. The sides and top are covered with $^1/_4$-inch sheet iron. It is very important that the cables, resistors and bricks are carefully protected from the action of the hot caustic. The cover of the pot consists of two cones of sheet iron with siliceous earth between them.

The construction of the resistors has proved excellent in practice. The coils can expand without impediment and can easily be interchanged by repairs. Through inspection holes in the walls the appearance of the resistors can be controlled. The division of the total resistance in several smaller units has the advantage that the temperature and rate of evaporation can easily be regulated and an eventual defect is localized to only a part of the whole system. Horizontal coils have also been tried. They are, however, more exposed to breaks than the vertical ones. The cost in Sweden for one 4-kilowatt resistor is as low as $10.50.

A great advantage of this furnace is that it can quickly be altered for the use of producer gas or other fuels, a matter of importance where energy is to be utilized which is not available at all times of the year.

The theoretical energy consumption by the finishing melting of caustics as calculated by the writer is as follows:

Caustic potash, 90 per cent KOH: 1.14 kilowatt-hours per kilogram = 0.52 kilowatt-hour per pound.

Caustic soda, 98 to 100 per cent NaOH: 1.63 kilowatt-hours per kilogram = 0.74 kilowatt-hour per pound.

The observed figure for 90 per cent caustic potash is 1.33 kilowatt-hours per kilogram or 0.604 kilowatt-hour per pound.

For caustic soda, melted under the same conditions, 0.86 kilowatt-hour per pound was the observed energy consumption. From these figures the energy efficiency of the furnace is found to be about 86 per cent.

The furnace construction as described or with suitable modifications can also be used for other heating and evaporation processes, at least to a temperature inside the pot up to 500° C., and probably higher.

Composition of Ozone and the Time-Energy Factor in Ozone Formation[1]

By Paul C. Saunders and Alexander Silverman

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

An ingenious apparatus is described in which oxygen is produced electrolytically, purified, subjected to a silent discharge in a modified Berthelot ozonizer, and then analyzed. All these units are included in a single all-glass train. Unusual care was exercised in the design and use of electrical measuring instruments. The ozone formed was determined by both titer and gas-volume changes in carefully controlled thermostats. The yield varied with time, energy input, and gap size.

The effect of a variety of voltages and current intensities was studied. A number of interesting relationships in results obtained is shown graphically. The study indicates that ozone may be formed over concentrated sulfuric acid with the same degree of accuracy obtainable in all-glass apparatus. This has the advantage of varying gas volumes in a single piece of apparatus instead of necessitating the construction of a large number of glass units of different capacities.

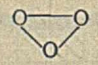
OZONE was discovered about 1785 by Van Maurum, a Dutch philosopher, who noticed a peculiar odor developed by his electrostatic machine. Cruickshank[2] in 1801 noticed the same phenomenon in the electrolytic preparation of oxygen from dilute acids. Schönbein,[3] in a memoir presented to the Academy at Munich, gave it the name "ozone" from the Greek, "I smell." The chemical nature of the gas was uncertain until Andrews and Tait[4] found it to be an allotropic form of oxygen. They examined the volumetric relations of oxygen and ozone, observing that when oxygen was treated with an electric discharge a contraction resulted and that heat destroyed it, giving the original volume. Also they observed that the iodine titer (the weight of oxygen equivalent to the iodine) of a sample corresponded in each case to the contraction that occurred in ozonizing it. Odling[5] (1861) observed these facts and that they were constant and assigned O_3 as the simplest formula. These interpretations were later supported by Soret[6] and Brodie.[7] According to Soret, when ozonized oxygen is allowed to act on turpentine, a contraction takes place due to the complete removal of the ozone. When a similar sample is heated to the complete destruction of the ozone, an expansion occurs which is one-half of the former contraction. Hence it is inferred that three volumes of oxygen produce two volumes of ozone.

Other attempts to verify the formula O_3 have been made by density and diffusion methods. Otto[8] made density determinations and showed ozone to have 1.5 times that of oxygen. Soret, by transpiration through a small aperture, applying Graham's diffusion law, came to the same conclusion.[9] Ladenberg, working with the explosively unstable liquid oxygen-ozone mixtures, has obtained a value of 1.3698 for an ozonized oxygen containing 86 per cent ozone. Also by the effusion method he obtained as a mean in five determinations a value of 47.78 as the molecular weight of ozone.

Theory

Ozone is produced in various ways, the chief methods being chemical, thermal, electrolytic, and silent electrical discharge. The last named includes such methods as glow, flame, brush, spark, and arc discharge. The silent discharge is usually employed. There is no unanimity of opinion regarding the number of oxygen atoms in the ozone molecule. Pure ozone has not been obtained, so the usual molecular weight determinations have been inapplicable. To quote Vosmaer, "We do not say ozone is O_3 but we say O_3 is ozone." This gives opportunity for naming the substances O_4 and O_6.

Ozone usually has assigned to it the graphic formula



but objection has been raised to this because all atoms would possess the same value and this equality suggests a stable rather than an unstable substance. Because of its peculiar oxidizing qualities in most reactions it may possess an unsymmetrical arrangement $O = O = O$, where one oxygen atom is tetravalent. A study of ozone reactions shows something of

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[1] Received June 13, 1927. Submitted to the graduate faculty of the University of Pittsburgh by Paul C. Saunders in partial fulfilment of the requirements for the doctor of philosophy degree.

[2] *Nicholson J.*, **4**, 245 (1801); *Gilbert Annal.*, **7**, 88 (1801).

[3] *Proc. Roy. Soc.* (*London*), **3**, 226 (1840).

[4] *Ibid.*, **10**, 427 (1859).

[5] *Proc. Roy. Inst. Gt. Britain*, **6**, 386 (1872).

[6] *Compt. rend.*, **61**, 941 (1865).

[7] *Phil. Trans.*, **44**, 435 (1872).

[8] *Compt. rend.*, **124**, 78 (1897).

[9] *Ber.*, **34**, 2282 (1900); **34**, 631 (1901).

the nature of the above suggested forms. The following standard reactions

$$O_3 + 2KI + H_2O = O_2 + 2KOH + I_2$$
$$O_3 + 3SO_2 = 3SO_3$$

show two ways in which the ozone molecule breaks down. The activity of the reacting substance may determine how the reaction goes, regardless of the ozone structure. Sulfur dioxide and potassium iodide by nature of their chemical properties show two distinct actions when activity is considered. Another interesting reaction is the effect of heat on the ozone molecule itself. At 200° C. complete disruption of the molecule occurs according to $2O_3 = 3O_2$

The electronic conception can be used to explain the formation of ozone by other methods, for all probably consist of electronic and molecular collisions. Ozone is formed by sending silent electric discharges through oxygen. When the electrical intensity of the surface of the electrode reaches a certain value, the electricity leaks into the gas and causes molecules of O_2 to become ionized.

Thomson[10] has shown that at least nine different substances are formed when a discharge passes through oxygen. Lenard[11] says that ionization of the air may be due to light waves striking solid particles in suspension. Townsend and Warner[12] claim that if gas molecules break up into ions as the result of ionic collision an increase of pressure should result. This pressure increase has been noted. With oxygen, however, no appreciable pressure increase has been noted when ozone is formed. The amount of ozone formed is a function of current, voltage, and frequency. The current passing through a gas is proportional to the average velocity of the ions and not to the kinetic energy of each ion. Otherwise the yield of ozone per coulomb would be greatly increased with high voltage. Warburg and Kabakjian[13] have contributed important data on this phase of the work.

If ozone formation is an electronic phenomenon due to molecular collisions, one molecule might be assumed to be formed by the transfer of one electron. If the molecular weight is assumed as 48, this number of grams should be formed for a current consumption of 96,540 coulombs, or 0.0005 gram per coulomb. Rideal[14] notes that the production per coulomb may be as great as five hundred times this value. Franklin[15] says the ultimate theory of the electrical formation of ozone is obscure and the process is one of ionization and recombination.

In recent years the production of ozone has attracted much attention from its commercial applications and considerable work has been done on the development of commercial ozonizers. The influence of capacity, self-induction, dielectric materials, current density, frequency, heat relations in the formation, and many other conditions and influences present problems which have as yet not been solved.

Purpose

The early history of ozone offers little information as to its physical constitution. A survey shows that our knowledge is very meager. The existence of "oxozone," the idea of activated oxygen possessing the so-called ozone chemical properties and not the physical constitution, and the fact that this allotrope of oxygen is produced in varying quantities in a silent discharge gap all offer problems of research vital to chemical and physical constitution.

It does not follow that in the volume contraction of oxygen by the silent discharge and the subsequent analysis of ozone we can definitely settle upon a molecular formula of O_3. A small quantity of oxozone (O_4) could very easily escape detection in view of the fact that only a small percentage of oxygen contracts into higher oxygen aggregations. Traces of O_4 and O_6 could easily escape detection, being masked by experimental error. Therefore, the true nature of ozone is not definitely known and the formula O_3 cannot be applied with certainty.

The first phase of the problem was to devise an apparatus for the production of ozone by the silent discharge, to study the oxygen-ozone pressure and volume relationships, and to make quantitative determination of the ozone thus formed. The second phase was to study the energy relations in ozone formation, the time factor, the influence of the polar gap discharge space, and the maximum ozone formed in oxygen-ozone equilibria under various conditions.

Apparatus

A modification of the Berthelot type of apparatus was used (Figure 1). It consists of a graduated glass tube, X_3, of 3 cm. diameter and 40 cm. length, which is surrounded by an outer jacket, X_1, filled with dilute sulfuric acid. Extending into the glass tube is another tube, X_2, of smaller diameter, also filled with dilute sulfuric acid. There is thus formed a gas chamber of definite width between the two acid layers. Metal electrodes of platinum are inserted into these acid tubes at T_3 and T_4. It was later found desirable, in order to avoid heating and sparking in the tube between T_3 and T_4, to change the platinum electrode T_3 to a tube protruding from the outer acid jacket at S_6 by making a rubber connection extending up beside and parallel to O_3. Now by connecting T_3 and T_4 to the secondary of an induction coil or other high voltage and frequency devices, a silent discharge is made to pass across the gap in X_3. Jacket X_1 is of glass and is glass-sealed to the tube X_3 at points of contact. The middle chamber, X_3, which has a known volume, is calibrated to tenths of cubic centimeters between the stopcocks S_7 and S_8. When oxygen fills the chamber and a silent discharge passes, a contraction in volume is registered by the manometer, M, which

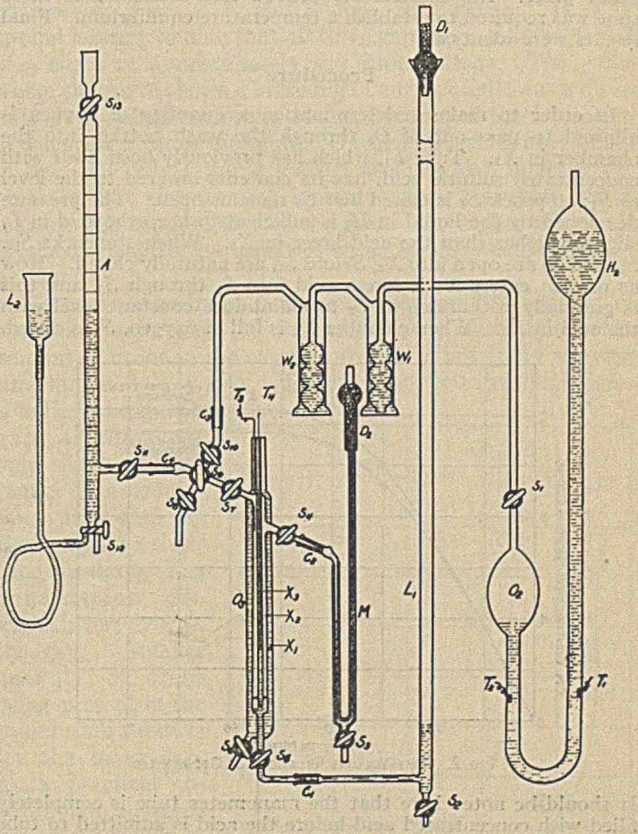

Figure 1—Apparatus for Generation and Analysis of Ozone

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[10] *Chem. News*, **103**, 265 (1911).

[11] *Ann. phys.*, **3**, 298 (1900).

[12] *Proc. Roy. Soc.* (*London*), **40**, 340 (1886).

[13] *Ann. Physik*, **13**, 464, 477 (1904); *Phys. Rev.*, **31**, 122 (1910).

[14] "Ozone," p. 104 (1920).

[15] *Proc. Am. Inst. Elec. Eng.*, **31**, 597 (1912).

contains concentrated sulfuric acid. Because of the destructive action of ozone on organic substances all connections were made of glass and glass ground joints were inserted at C_1, C_2, C_3, and C_4.

Pure oxygen was prepared electrolytically from dilute sulfuric acid, the oxygen coming off at the anode T_2 and collecting in the reservoir O_2 of 600 cc. capacity. The hydrogen forming at T_1 escaped up the right arm into the room. In order to destroy any ozone formed in electrolysis, the oxygen was passed through bulb W_1, containing alkaline potassium iodide. It was then dried by concentrated sulfuric acid in bulb W_2 before passing to the ozonizer X_3, through stopcocks S_{10}, S_9, and S_7. The tall tube, L_1 (5 feet long), contained concentrated sulfuric acid and served to push the ozonized oxygen out of the chamber X_3 into the graduated analyzing tube, A, which contained 0.1 N potassium iodide solution. The ozone reacted with the potassium iodide, liberating iodine and oxygen. The liberated oxygen was then measured over the displaced solution, a part of which flowed into the leveling cup, L_2. The amount of iodine was then determined by 0.01 N sodium thiosulfate. Calcium chloride tubes, D_1 and D_2, kept the moisture content of the acid at a minimum. Ozone, which is practically insoluble in concentrated sulfuric acid,[16] is appreciably soluble in water and even reacts with saturated hydrocarbon oils. Results obtained over concentrated sulfuric acid were identical with those obtained in glass alone.

All capillary connections are of 1-mm. bore. Stopcock S_9 is three-way, making connections with the oxygen line through S_{10}, and opens directly into the room at S_8, thus serving to flush the extremities of the apparatus before taking in a new charge of oxygen. The ozonizer is disconnected at the glass ground joints C_4, C_3, and C_1, but left connected with the manometer at C_2 and inserted in an electrically controlled thermostat, containing distilled water, at room temperature after which electrification takes place. Air thermostats proved less desirable, as more time was required to establish a temperature equilibrium. Final results were identical.

Procedure

In order to make a determination a quantity of oxygen is allowed to pass out of O_2 through the wash bottles into the chamber in X_3. Tube L_1, which has previously been filled with concentrated sulfuric acid, has its contents lowered to the level of S_7; stopcock S_4 is closed and S_5 remains open. The pressure developed by the liquid in H_2 is sufficient to keep the acid in L_1 slightly higher than the acid layer in X_3. When stopcocks S_{10}, S_9, and S_7 are open into X_3, S_8 and S_{11} are naturally closed. Now as oxygen enters X_3 it forces acid into L_1 through S_5, and this is gradually withdrawn at S_2 to maintain a constant level with the acid in X_3. When chamber X_3 is full of oxygen, S_7 is closed.

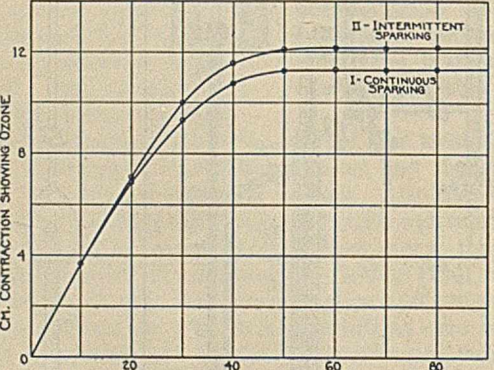

FIG. 2. TIME-VOLUME RELATIONS OF OZONE YIELD

It should be noted here that the manometer tube is completely filled with concentrated acid before the acid is admitted to tube X_3. The levels in M are adjusted to some convenient point midway between top and bottom by letting out surplus acid at S_3, drawing a small quantity of oxygen from X_3 into the capillary through S_4 and simultaneously securing a constant acid level in L_1 and X_3. The fact that the acid layers are the same in both arms of the manometer M indicates that the oxygen is at atmospheric pressure. S_5 is now closed.

The silent discharge passes through the oxygen and the volume contraction is read off on the manometer. After coming to constant temperature the gas, which now contains some ozone, is slowly passed into A by running acid into the lower gas chamber from L_1 through S_5. Corrections are made for capillary volumes in all determinations. As the ozone enters the potassium iodide solution, iodine is liberated, which is later determined by thiosulfate. All gas volumes are reduced to normal temperature and pressure conditions in the dry state.

The apparatus sketched in Figure 1 was used for the study of both ozone composition and the time-energy relations. Ozone was first formed by a silent discharge from an ordinary induction coil. Later it was produced by a testing transformer which was connected to the city lighting circuit of 110 volts and 60 cycles.

Quantitative Determination of Ozone

Among several methods for the determination of ozone the one commonly used utilizes a weak potassium iodide solution with a standard thiosulfate solution. The two common reactions are

$$O_3 + 2KI + H_2O = I_2 + O_2 + 2KOH$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

The reaction takes place in neutral solution. Before titrating with thiosulfate the potassium iodide solution is made slightly acid with sulfuric acid, to avoid the formation of potassium iodate in the newly formed alkaline solution.

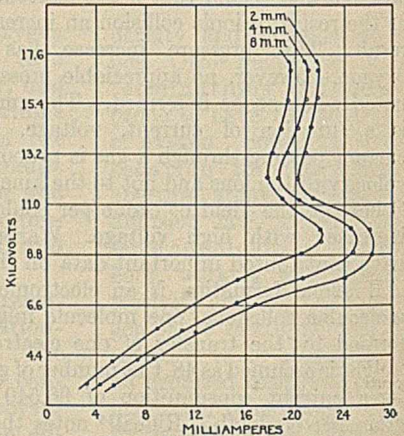

FIG. 3. - VOLT-AMPERE RELATIONS GAPS 2, 4, & 8 m.m.

Electrical Instruments and Measurements

It is not easy to make accurate electrical measurements. Not only is there lack of instruments, but upon search for advice there is a remarkable lack of available information. The problem in this research was to obtain an ammeter which would measure current across a gas gap of several millimeters length furnished by an alternating current, and a voltmeter to measure the potential difference required for this current in the formation of a silent discharge. The current in the gas gap follows Ohm's law until the rate of removal of gas ions reaches the so-called saturation current, at which point it appears to be independent of the voltage applied. Large currents cause the gap to become more conductive and the glass connections to become heated, ending finally in spark discharges.

The potential difference was first determined by the length of the gap between two electrodes across which the given voltage would just cause a spark to pass. This form of voltmeter, consisting of two brass balls, was connected in parallel across the spark gap of the ozonizer. In the transformer the voltage can be determined if the transformation ratio is known. A final control on the potential difference can be obtained by measuring the current in the secondary and the energy input in the primary by a wattmeter.

An induction coil was first used to make ozone, but serious difficulties were encountered when the measurement of the energy relations was undertaken. A 3-kilovolt-ampere, intermittently rated, 30,000-volt testing transformer was then chosen to furnish the potential. It contained an induction regulator, a circuit breaker, a voltmeter coil for reading the high-tension voltage, and a dial connected to the induction regulator from which the voltage could be accurately

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[16] *Z. Elektrochem.*, **18**, 129 (1912).

read. The induction regulator permits of the gradual raising of the voltage without causing surging or wave distortion. By means of a multiple series connection the transformer could be operated from a 110- or 220-volt circuit and 25 or 60 cycles. The transformer could be operated continuously for periods when very small loads were drawn, as in this research. The instrument was calibrated and corrections applied, including power factor determinations.

The problem of measuring a very small alternating current of high frequency offers the serious difficulty of inductive circuits which are functions of frequency. It could not easily be predicted what current would pass a gap of 2 to 8 mm., so the process of trial and error was used until the right instrument was discovered. A vacuum thermocouple was found to be satisfactory. It measures the effective or root mean square value of an alternating current and with wide limits the accuracy is independent of the frequency.

Composition of Ozone

Table I shows the results of ozone formation without special regard to the conditions under which it was produced.

Table I—Composition of Ozone in the Initial, Final, and Titer Values Mixed with Oxygen

I	II	III	IV	V
Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*
44.57	43.81	44.00	0.76	0.77
45.30	44.40	44.55	0.90	0.83
46.50	45.24	44.57	1.26	1.25
46.62	45.39	45.09	1.23	1.34
47.20	45.90	45.60	1.30	1.32
		Mean	1.09	1.102

Column I shows the initial volume of oxygen drawn into the ozonizer.

Column II shows the volume mixture of oxygen and ozone after the silent discharge has passed, the contracted volume being computed by the changes in the sulfuric acid column in the manometer tube.

Column III represents the volume of oxygen remaining after the ozone has reacted with the KI solution.

Column IV shows the contraction due to ozonizing the oxygen and the values are the differences of columns I and II. It shows the contraction by computation.

Column V, the titer value (cc. of oxygen equivalent to the iodine liberated), shows by chemical analysis the amount of ozone formed. The titer is obtained in terms of 0.1 *N* thiosulfate by multiplying the number of cubic centimeters of thiosulfate by its oxygen equivalent. One cubic centimeter of 0.1 *N* sodium thiosulfate is equivalent to 0.0024 gram of O_3 or 0.56 cc. of O_2 at normal temperature and pressure.

One striking result is to be noted. The computed volume contraction in column IV is approximately equal to the titer value of column V. The above titer value was determined by the equation

$$O_3 + 2\,KI + H_2O = O_2 + 2\,KOH + I_2$$

where one atom of oxygen in the ozone is equivalent to I_2. A sixth column in Table I might have been made, in which the contraction (the difference between columns I and III) would serve as another check on columns IV and V. Such computations were attempted, but the results were not conclusive. The large deviations were probably due to fluctuations in solubility and heat of solution when the ozone reacted with the potassium iodide solution. The accuracy of this method is based upon Houzeau's[17] modification of the iodine method, which is extremely accurate. Many runs were made under various voltages and time lengths which showed no general deviation from the results in Table I. Therefore, it appears that ozone has the formula O_3, even though there is an error in columns IV and V amounting to about 1 per cent. This error was also observed in all-glass apparatus so it cannot be attributed to the confining liquid (concentrated H_2SO_4) in the ozonizer.

Energy Relations

One of the first determinations was based on obtaining the maximum amount of ozone in equilibrium with oxygen by passing a silent discharge through oxygen. Figure 2 shows the time-volume relationship of ozone yield. The confined oxygen was ozonized for increasing time periods. Curve I represents the equilibrium conditions for continuous sparking and curve II for intermittent sparking, consisting of 10-second runs with 5-second periods of intermission, and the time as plotted being the sum of the actual sparking periods. Both curves show that equilibrium is established between O_2 and O_3 when the two gases are confined in the same space. The intermittent curve rises higher because more ozone is formed. This may be due to the fact that heat is generated constantly in the continuous discharge, while with intermittent sparking there is periodic cooling in the thermostat, which insures a greater ozone yield. It seems probable that if the charging periods were made less than 10 seconds the curve might rise even higher.

Ozone does not form in appreciable quantities until a certain voltage is applied, and this varies according to the size of the gap. A purple glow accompanies the incipient ozone formation with a purring noise. Heat effects accompany all glow discharges and have much to do with the yield. Pure, fresh, dried oxygen gives a quicker yield, but the ozone decomposes more rapidly than that prepared from oxygen which has been allowed to stand over concentrated sulfuric acid or water.

Figure 3, a peculiar curve, shows how the current varies with the voltage for the three ozonizers whose gaps or discharge spaces are 2, 4, and 8 mm., respectively. It is of special interest to note that all three gaps give the same sort of a curve at approximately the same voltage. The point where the curve shows a lessening of current indicates a diminution of ionized molecules of gas, because of the formation of the neutral ozone molecule. Oxygen molecules may break in two, not only forming ionized atoms which increase the pressure, but also forming ionized oxygen molecules which increase the conductivity of the gas. The higher potentials produce arcing in the ozonizer, so no further readings could be taken.

Figure 4 shows by percentage contraction (the amount of ozone is proportional to the manometric contraction) the amount of ozone in the oxygen-ozone mixture under varying time limits: $3\,O_2 = 2\,O_3$. The mean current in milliamperes is indicated for each gap, as there are only slight fluctuations. The contraction varies with the time only for a short time duration. The contraction also varies inversely with the gap, a smaller quantity of ozone being present in the equilibrium mixture for the larger gap. As a practical application of these curves, one should study their lower portions. Here it is observed that for a given time much more ozone results with the smaller gap. Depending upon the rate of flow of gas through an ozonizer, the amount of ozone can easily be computed. One minute of ozonizing with the 2-mm. gap furnishes two and a half times that obtained with the 4-mm. gap. The equilibrium point is reached sooner in the smaller gap, or the gap that furnishes the greater yield. These

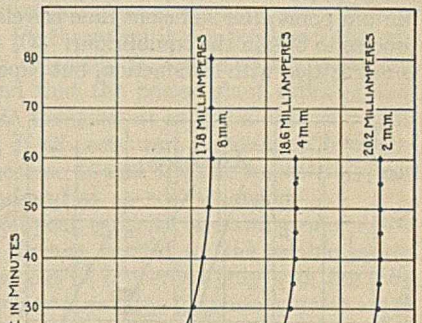

FIG. 4.—CONSTANT VOLTAGE 12,100.

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[17] Annuaire de la Societe Meteorologique de France, 5, Pt. 2, 43 (1857).

equilibrium points are mostly due to heating effects, the larger gaps offering greater resistance with consequent ozone destruction through heat.

The percentage-contraction term should not be confused with the maximum percentage of ozone, although the two values are proportional. The percentage ozone formed by weight is three times the percentage of contraction. The equation $3O_2 = 2O_3$ shows this; when 100 per cent ozone forms, the contraction is 33 $^1/_3$ per cent.

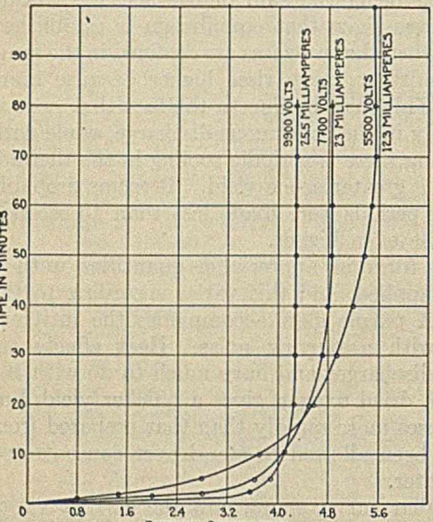

FIG. 5-YIELD-TIME RELATIONS CONSTANT GAP 2mm.

Figure 5 shows the yield-time relation with a constant gap and varying voltage. The current was a practical constant for a given curve. As the equilibrium is reached, the highest voltage curve, which showed the greatest rate of yield at first, indicates the least ozone. The lower the voltage applied, the slower the rate of ozone formation; but the higher the ozone content at the equilibrium point. Of course, the time factor enters here. These yields are doubtless the result of heat effects. If the temperature could be maintained constant, or the period of discharge made shorter, thus avoiding all heating effects, the higher voltage curves would move to the right and eventually coincide in the upper parts with the lower voltage curve. It is evident that the higher voltage is more efficient from the commercial-yield standpoint because, practically, the gases would be swept out of the ozonizer in less than a minute of time.

Figure 6, which has been indicated in Figure 5, shows the study of the effect of the voltage on the oxygen-ozone equilibrium point after sufficient time has elapsed in the discharge process to obtain the equilibrium: $3O_2 = 2O_3$. The problem is not settled with satisfaction, but experimental results have been obtained. No regard to the amount of time was considered. However, it compares with the results in previous curves. It has been conclusively demonstrated that as the voltage is increased the ozone content, at equilibrium, is less. The explanation is that of heat effects. The curves for each gap are limited to the range between the incipiency of ozone formation at the lower voltages and the heating effects and arcing at the higher voltages.

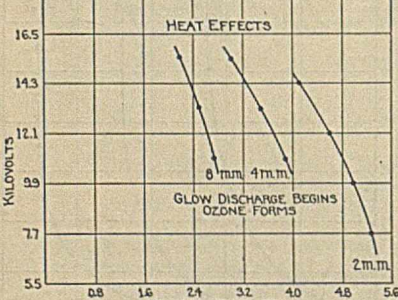

FIG. 6-VOLTAGE-MAXIMUM OZONE AT OXYGEN-OZONE EQUILIBRIUM $3O_2 \rightleftarrows 2O_3$

It is of commercial interest to know the relationship between energy input and ozone yield under the varying conditions of manufacture. The study of such a curve (Figure 4) shows certain relations already mentioned. Figure 7 shows the relation of the ozone in grams per kilowatt hour to the size of the gap. A yield of 4 to 50 grams of ozone per kilowatt-hour is low compared with the commercial type of ozonizer, which gives 30 to 40 grams for air and three times these values for oxygen. Yet it is well to note that the Berthelot type is a fairly efficient machine besides being simple in design and easily portable for laboratory use. The yield of ozone varies inversely as the gap.

The influence of voltage on ozone yields has been a subject of much discourse. Chassey[18] claimed for a fixed air gap that there was an increasing linear relationship between ozone yield per ampere hour and the potential applied. Warburg, Gray,[19] and Kabakjian[20] all found that after the brush discharge was fully established the yield per coulomb was independent of the voltage for a given gap. Data from this research taken for the three gaps verify these statements in part. (Table II) The glow discharge must first be established before the yield per coulomb becomes constant. Ozone production is independent of the voltage applied within certain limits, but the higher voltages produce heating effects with the consequent destruction of ozone. Therefore, the results of this investigation imply that the yield per coulomb increases with voltage, then remains constant through a range which terminates where heating of higher voltages reverses the reaction and lowers the yield.

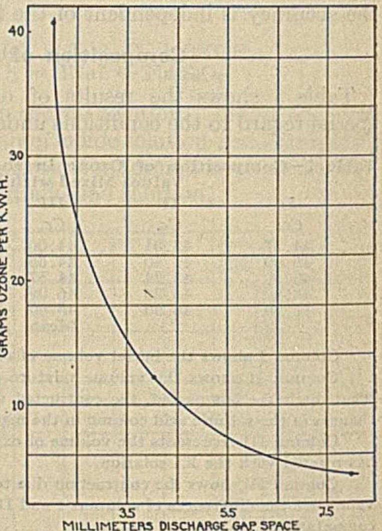

FIG. 7 YIELD-GAP RELATIONS FOR 13,200 VOLTS

Table II—Ozone Yield Per Coulomb

Volts	*Milliamperes*	*Grams O_3 per coulomb*
	2-MM GAP	
6,600	16.7	0.0018
11,000	21.4	0.00227
12,100	20.1	0.00262
13,200	20.7	0.00257
15,400	21.8	0.00206
	4-MM. GAP	
9,900	24.7	0.00100
11,000	20.3	0.00139
12,100	18.4	0.00198
13,200	19.5	0.00197
14,300	20.3	0.00195
16,500	21.4	0.00175
	8-MM. GAP	
13,200	18.0	0.00112
14,300	18.7	0.00129
15,400	19.5	0.00120
16,500	19.5	0.00101

Conclusions

1—The formula for ozone under the conditions studied is apparently O_3.

2—With constant amperage, voltage, and gas gap the oxygen-ozone equilibrium is apparently the same for both continuous and intermittent discharge up to a certain time limit, when it becomes greater for the intermittent discharge.

3—For a constant amperage, voltage, and gap the yield is a linear function of time for a short period before the equilibrium point is reached.

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[18] *Compt. rend.*, **134**, 1298 (1902).

[19] *Ann. Physik*, **13**, 464 (1904).

[20] *Physic. Rev.*, **31**, 17 (1910).

4—The maximum oxygen-ozone equilibrium varies inversely as the voltage for a given gap—that is, the higher the voltage, the lower the ozone content at the oxygen-ozone equilibrium.

5—For a given gap the yield per coulomb is constant and independent of the voltage after the true brush discharge is established.

6—Disregarding the energy input, the percentage yield of ozone varies inversely with the size of the gap.

7—The yield of ozone per unit of energy input is an inverse function of the gas gap employed.

8—The maximum contraction of gas volume in this investigation was 5.5 per cent (ozone yield = 16.5 per cent) at 5500 volts and 12.3 milliamperes with a 2-mm. gas gap.

Hydroelectric Fuel[1]

Water Power Applied in Fuel Utilization

By A. T. Stuart

8 Strachan Ave., Toronto, Canada

Nearly half of the available energy from the heat generated by the combustion of various solid, liquid, and gaseous fuels comes from their hydrogen content. Hydrogen gas has been a familiar commodity ever since the introduction of artificial fuel gases, which generally carry approximately 40 per cent elemental hydrogen. It can be said, therefore, that hydrogen is a basic commodity perhaps doubly valuable as an elemental gas.

Fuels have always been burned in natural air, which carries about 80 per cent of diluent gases, and it is not often realized that in burning 1 ton of coal we often use as much as 14 tons of air containing 10 tons of diluents. The presence of these diluents lowers temperatures and causes enormous wastages in fuel. It is not surprising, therefore, that of late the technical literature[2] draws attention to the fact that cheap oxygen would permit of almost revolutionary advancement in industry and that some one hundred leading industrial technicians have discussed the possibilities of its universal application.

Economic Considerations

Oxygen at 25 cents per 1000 cubic feet would generally be accepted as of low cost, but it might be shown that this expression "low cost" is so flexible that oxygen at $1.00 at certain points for specific processes may be quite as attractive as oxygen at 10 cents under other circumstances. However, at present there is no apparent prospect of oxygen being separated from air at costs as low as 25 cents per 1000 cubic feet.

The various writers have dismissed consideration of water as a source of low-cost oxygen with the statement that power requirements are excessive and that cheap power is not generally available. But, contrary to the usual point of view, it could be argued theoretically that the production of oxygen from water requires no expenditure of energy since the electrical energy consumed reappears as the energy of hydrogen which is generated from water along with oxygen. Such hydrogen, at least as a fuel gas, is universally usable and for this and many other purposes its value will, in many regions and circumstances, provide oxygen at costs under 25 cents or at no cost whatever.

Since both hydrogen and oxygen, whenever available at low cost, can find simultaneous and general use in industry, it is only necessary to indicate the proper circumstances of production to permit of the extensive use of these gases to effect large economies in metallurgical, ceramic, gas-making, and gas-consuming industries in such regions.

With suitable apparatus, from one continuous horsepower year of direct-current power there can be generated 60,000 cubic feet of hydrogen and 30,000 cubic feet of oxygen. Consequently, for each $1.00 charged to this power the cost of each gas totals 1.11 cents per 1000 cubic feet. Aside from power all other costs need never exceed 5 cents per 1000 cubic feet.

Since it can be shown that both gases can find simultaneous and unlimited utilization at many power locations, an operating company can generate power largely or entirely for such purposes. The cost of developing water power at the site averages at the present time about $15 per horsepower, with the tendency for such costs to reduce with the fall in money rates. Even steam power can be generated on a high load factor at costs comparable to the above when the plant can be ideally located with regard to coal and water supplies or the exhaust from turbines can be utilized and charged to other processes. With such power costs the gases can be delivered from the generating plant at approximately 23 cents per 1000 cubic feet. Furthermore, it can be shown that the electrolytic process is especially favorable to the utilization of off-peak power and that the power plant utilizing such capacity may generate the gases at as low a cost as 5 cents per 1000 cubic feet. If all costs were imposed on hydrogen its cost would then become 35 and 8 cents, respectively, and oxygen would be produced at no cost whatever.

In utilizing unsold off-peak capacity on water-power plants, the cost of which is already carried by the salable power, the power company would be concerned only with the costs of operating the necessary apparatus for making gases. Off-peak power would be divided into various blocks. First there would be that relatively small block available over 95 per cent of the hours of the year, a second and larger block available 90 per cent of the hours, and so on to the largest block available, perhaps less than 50 per cent of the hours. The cell plant would be operated almost constantly throughout the year, taking an overload of tenfold for perhaps 50 per cent of the time to a normal high-efficiency load production for perhaps 10 per cent of the time. With these variations in capacity of from one to ten there would be variations in efficiency of production per horsepower year from 90,000 cubic feet to only 60,000 cubic feet, but with only minor power charges or none at all this alteration in efficiency is not important. It is pointed out below that such seasonal

[1] Received May 14, 1927.

[2] Hodsman and Cobb, *Gas J.*, **150**, 640 (1920); Finlayson, "Industrial Oxygen," Woodall-Duckham Co., 1923; Willien, *Am. Gas Assocn. Monthly*, **5**, 565 (1923); Vandaveer and Parr, This Journal, **17**, 1123 (1925); Parsons, *Intercol. Gas J. Canada* (1922); Jeffries, *Gas Age*, February 25, 1921; *Bur. Mines, Repts. Investigations* **2502** (1923); Johnson, "Principles, Operation, and Products of the Blast Furnace," p. 532; Unger, address before American Iron and Steel Institute, June, 1922; Cottrell, paper before American Iron and Steel Institute, May, 1920; *Trans. Am. Inst. Mining Met. Eng.*, **13775**.

and daily variations in production of oxygen and hydrogen at exceedingly low costs can be absorbed industrially.

Pure electrolytic hydrogen may often have especially high values for such processes as the hydrogenation of animal, vegetable, and mineral oils, for the hydrogenation of coal, the fixation of nitrogen, the reduction of pure metals from ores, the syntheses of various alcohols, aldehydes, and hydrocarbons not to mention its value merely as a constituent of artificial fuel gas. The value of such hydrogen will, of course, vary tremendously with regions and circumstances and may be considerably over $1.00 in special cases. Generally speaking, its value (even its holder value in town gas plants) when produced under favorable conditions may not be less than sufficient to provide oxygen as a by-product either at no cost or bearing a cost under 10 cents per 1000 cubic feet. Since hydrogen can find use almost anywhere at such values, we then have a means of producing no-cost or low-cost oxygen wherever water power or cheap power is available.

As indicative of the resources in water power still available even in the United States, the report of the Federal Power Commission shows that 44 million maximum horsepower still remain to be developed. In addition it is safe to conclude that a study of load curves on the 11 million horsepower plants already operating might indicate that 25 per cent of this capacity is not fully utilized or sold. Further, in addition to water power, cheap power can sometimes come from steam plants under circumstances already noted. Accordingly the sources of cheap power may be widely scattered in any country.

Although low-cost oxygen and hydrogen could best be produced in large quantities at the power plant, production might also be effected at any point on the electric transmission system or even on the premises of customer industries. If produced at the power plant, the oxygen and hydrogen could be fully utilized there in various processes, or these gases or gaseous products of manufacture could be distributed in pipe lines over large areas.

It is not necessary to comment on the uses of hydrogen, especially its use as a constituent of fuel gas. Aside from its use as a fuel, the demand for hydrogen in a more or less pure state is growing enormously and it is estimated that, with the operation of plants now projected, the demand will total over 100 billion cubic feet per year. With the introduction of new processes, such as the Bergius process for the hydrogenation of coal, and the use of hydrogen as a reducing agent for metallic ores, this demand will know no limit especially when all surplus supplies can be absorbed in gas works.

The potential uses for oxygen may be divided into two main categories. By the first process it is possible to produce from coal solid, liquid, and gaseous products containing almost 100 per cent of the energy values of the coal consumed. By the second process these products could be burned in atmospheres enriched with oxygen to any desired degree. Thus, too, the potential uses for oxygen are likewise unlimited.

In regard to possible production of oxygen and hydrogen, it is only necessary to remember that water is the raw material and that each 1 horsepower year can produce 90,000 cubic feet. While the generation and utilization of enormous quantities of these gases would involve no radically new principles, this very circumstance makes the matter the more attractive and raises the question as to why nothing has been done industrially along these lines heretofore. The potential importance of the application of the electrolytic process to basic industry may therefore be summarized.

Gas Works

Oxygen permits of the simplest form of gas-making equipment for the production of rich gases from coal—a brick-lined shaft furnace internally and continuously fired by an oxygen-steam blast. No grates would be necessary since the temperature at the base of the shaft could be so regulated that the ash would fuse and could be tapped out. The apparatus and process would resemble somewhat the industrial gas producer operated on air and steam. One such stack could supply the usual needs of a medium-sized city, since authorities have estimated that 1 ton of bituminous coal could then yield some 62,000 cubic feet of 400-B. t. u. gas. Adding to this the electrolytic hydrogen, the yield becomes 87,000 cubic feet of 385-B. t. u. gas, or 335 therms per ton of coal.

Such production may be compared with some ordinary gas-works practice. As an example, the gas production of one large plant averages less than 100 therms per ton of coal purchased, not to mention the gas oil consumed in addition to the coal. It is true that such a plant also sells gas coke for domestic users, but domestic coke can hardly be considered the ultimate ideal fuel if cheaper gas were available. From the point of view of the production of gaseous therms the oxygen process can eliminate the purchase of gas oil and still reduce purchases of coal by about 70 per cent and provide gas low enough in cost to permit it to substitute all other forms of fuel.

The oxygen process would represent the ideal not only in complete gasification but also for the recovery of by-products. In the ordinary practice of gas works coal is heated in numerous small externally fired retorts, the walls of which are necessarily at higher temperatures than the charge within. Consequently, the delicate volatiles released from the coal at one temperature are forced along the hotter walls of the retorts to the exits and are thereby largely "cracked" into fixed gases and carbon.

In the internally fired stack described above the contrary is the case. The coal in descending is gradually heated by the ascending column of water gas generated by the oxygen-steam blast on the coke at the base of the stack. This water gas, being rich in hydrogen, provides the ideal atmosphere for the preservation of the volatile matter which, when once released from the coal, is swept upwards in the gas stream into cooler zones.

The recovery of valuable liquid fuels and gasoline substitutes by such means should exceed the best yields of any of the recently introduced low-temperature carbonization processes, where some 20 imperial gallons are obtained per ton of coal. In addition there would be recovered better yields in ammonia and low-temperature tars than in usual practice. All residues would be completely gasified, so that the various products would contain all the values of the coal consumed.

If 100,000 horsepower were used, about 240,000 tons of coal could be processed per year for the production of some 6 million gallons of oils and motor fuels, with yields in ammonia and tars, together with the equivalent of some 10 billion cubic feet of 350-B. t. u. fuel gases and 6 billion cubic feet of pure electrolytic hydrogen. With the proper use or disposal of the by-products from coal-processing, the fuel gases would be generated at very low cost. They could be piped long distances from power sites, as now undertaken from coal areas in Germany, and could effect large savings in the distribution and consumption of raw fuels in the form of anthracite, bituminous coal, fuel oil, coke, and expensive gas.

High-Temperature Combustion

Many industries use or are capable of using enormous amounts of fuel gases. Such requirements are met in part from producer gas made on the premises, and therefore the question is raised whether such an industry could use oxygen when cheap power is available and when low-cost gas does not reach the plant. From low-cost power delivered to the plant oxygen and hydrogen could be produced both for the complete gasification of coal and to economize in gas combustion. As already noted, the production of gas per ton of coal and 0.42 horsepower year of power would total 62,000 cubic feet of 400-B. t. u. gas and some 25,000 cubic feet of electrolytic hydrogen—making a mixture of 87,000 cubic feet of 385-B. t. u. gas. This compares with ordinary producer gas of 145-B. t. u. value and containing over 50 per cent of inert nitrogen. Owing to the higher flame temperature of gases free of nitrogen the fuel efficiency of a high-temperature industrial process would be vastly improved with the use of 385-B. t. u. gas.

When excessive flame temperatures are required in a process, ordinary practices are extremely wasteful and, while sometimes twenty-five times the theoretical fuel requirements are used, it is not unusual to find consumption running five to ten times the theoretical amount. As indicated, great improvement could be effected by providing 385-B. t. u. gas free of nitrogen, but there still remains the possibility of obtaining vastly greater economies from the use of oxygen in combustion when it is remembered that to burn 1 ton of coal as much as 14 tons of air, containing 10 tons of nitrogen, are used. The use of oxygen for air enrichment for gas combustion in high-temperature industrial furnaces might easily represent greater advantages than those possible when oxygen is used in gas-making, since economy would be effected in the use of finished gases at the point of consumption where usual wastage is far greater than that in gas-making.

Central gas works at water-power sites could meet the requirements of high-temperature industry by supplying in pipe lines both low-cost fuel gas and oxygen for its combustion. On the other hand, water-power plants could supply power, either continuous or off-peak, to such industries for making their own gas and surplus oxygen for combustion. The possible economy in coal could then easily reach 66 per cent in many metallurgical and ceramic industries, and to this could be added economy in fixed charges and labor and in improvement in products. Indeed, the command and exact control of low-cost high-temperature heat would permit of the introduction of new products and processes unknown at the present time.

Water-Gas Syntheses

Water gas, containing equal volumes of carbon monoxide and hydrogen, is now being used for special purposes, such as the synthetic production of various alcohols and hydrocarbon oils and gasoline substitutes from coal by the Fischer, Patart, Audibert, du Pont, and other processes.[3] It is also a convenient source of hydrogen for other purposes and therefore the production of water gas with oxygen is a matter of first importance.

By processes and apparatus similar to those described for the complete gasification of bituminous coal, coke may be gasified by an oxygen-steam blast at almost 100 per cent over-all thermal efficiency. The product gas would be free of inerts and would contain approximately two-thirds carbon monoxide and one-third hydrogen, but if the equivalent electrolytic hydrogen were included the volumes would of course become equal. For each horsepower year and approximately 2.15 tons of coke the product would total close to 240,000 cubic feet of 320-B. t. u. gas free of inerts and would represent a saving of up to 6 tons of bituminous coal over usual practice.

However, coke is an expensive commodity as made by usual methods. Hodeman and Cobb have studied the production of coke in a gas producer as described above by means of internal firing with the oxygen-steam blast. They estimate that some 53.3 per cent of the heat of the coal used will appear as the heat value of coke, 31.6 per cent will be the heat content of gases, and 9.26 per cent will be the heat in tars. The gases were estimated at 20,000 cubic feet of 427-B. t. u. value and from them could be recovered liquid fuel and ammonia as noted previously. With the recovery and sale of such products and in view of the high efficiency of the oxygen process of making coke, the credits might be such that coke would become a free by-product.

There is no apparent reason why coal could not be processed in a single operation and apparatus for the recovery of all by-products and the extraction of water gas equivalent to 53 per cent of the weight of the coal consumed. Based on the above estimates, the yield of water gas, including electrolytic hydrogen, may then total per ton of coal some 60,000 cubic feet of 320-B. t. u. gas free of inerts together with by-products in condensable oils, tars, ammonia, and small amounts of fuel gas of high B. t. u. value. In view of the simplicity of the process from coal to water gas and in view of the high credits, the water gas so produced may figure at only negligible cost and represent large economies in the usual demand for coal.

Hydrogen Production

Hydrogen is required in large amounts for synthetic ammonia, the hydrogenation of animal and vegetable and mineral oils, the liquefaction of coal by the Bergius[3] process, dirigibles, etc., and may shortly be required for new processes such as the reduction of ores to metal. Electrolytic hydrogen cheaply produced would, of course, be directly available for such purposes, but it would also be desirable to use oxygen in the production of further amounts of hydrogen rather than water gas. In present practice it is usual first to produce water gas from air and coke and later to convert this into equal volumes of hydrogen by the Haber-Bosch process or by the iron-sponge method, etc.

The possibility of at least partially effecting carbon monoxide conversion within the producer when oxygen is used becomes an interesting possibility in view of the principles of Mond producer practice. The Mond producer operates at very low temperatures and with large excesses of steam in order to favor these reactions:

$$C + 2H_2O = CO_2 + 2H_2$$
$$CO + H_2O = CO_2 + H_2$$

and as a consequence Mond gas is rich in hydrogen. It is reported in some recent articles that the reaction between steam and carbon at 500° C. produces hydrogen almost entirely in preference to carbon monoxide and that the reaction can be expedited by specially preparing coke free of tarry substances.

For each volume of oxygen consumed in such processes there would be produced six volumes of hydrogen in addition to the original two volumes of electrolytic hydrogen. Consequently, 1 horsepower year and 2.15 tons of coke might be capable of producing up to 240,000 cubic feet of hydrogen, of which 25 per cent would be electrolytic. This hydrogen would then be available for the purposes indicated, of which not the least interesting would be the reduction of iron from ores by hydrogen.

Reduction of Ores by Gases

Considerable attention and experimentation has lately been directed towards the gaseous reduction of ores. The process is peculiarly attractive and holds so many inherent ad-

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[3] Proceedings International Conference on Bituminous Coal, November 15 to 18, 1926, pp. 132, 234, 102; published by Carnegie Institute of Technology.

vantages over present methods of smelting with coke in blast furnaces that it seems that ultimately blast furnaces and smelters may be discarded and solid coke may be substituted by reducing gases. Although several authorities have discussed the use of oxygen for air enrichment in blast furnaces and have pictured future furnaces so operated, it can be argued that, rather than this, the future will see the reduction of ores by gases.

Gaseous reduction of ores largely hinges upon available supplies of low-cost reducing gases, such gases of course being carbon monoxide and hydrogen. Heretofore water gas made by usual methods has been the sole industrial source of reducing gases in quantity. The cost of water gas has so far not permitted serious consideration of its use as a reducing agent for such base metal as iron and as for hydrogen its cost has been prohibitive. Of the two gases hydrogen is, of course, the ideal reducing agent in that water, the product of the reduction, can be readily removed from excess furnace gases so that excess hydrogen could be recirculated. Some 20,000 cubic feet of hydrogen would be required per ton of iron, and in view of what has been previously discussed it is possible that hydrogen might become available for the reduction of ores.

An apparatus for the reduction of iron by hydrogen or water gas might take the form of a vertical pipe only a few inches in diameter and suitably heat-insulated. The middle section, constituting the reduction zone, could be heated electrically to not over 900° C., so that reduction would take place without fusion. The top unheated section would serve to dry and to preheat the descending ore while the bottom unheated section would cool the product and heat ascending hydrogen. When hydrogen is used the excess gases could be collected at the top, freed of impurities (such as H_2O, H_2S, PH_3) and the excess hydrogen could be recirculated. The reduced product, still solid, could be melted and fluxed by suitable electric means or by oxygen-fed flames. Such an apparatus has been operated with facility and with the production of several tons per day. Production seemed to be limited only by the rate of input of heat and hydrogen.

Some of the obvious advantages of the process include:

1—Iron could be produced from water power and without coke.

2—Electrolytic oxygen can be used to make six volumes of reducing gases, by means of the gas producer and coke, also for ore reduction.

3—The product of reduction is free of silicon, sulfur, phosphorus and carbon, and when melted and fluxed of gangue would be virtually high-grade steel directly from ore.

4—Phosphorus, now lost in slag, could be recovered from furnace gases.

5—There would be no waste heat and no waste gases.

6—Ore might be smelted at mines and shipments limited to metal only.

7—The reduced powders are convenient for storage and shipment.

8—The apparatus would be of negligible first cost and, if desired, could be operated seasonably to use off-peak power or to balance gas production for winter heating.

A 100,000-horsepower plant would then produce sufficient electrolytic hydrogen for the production of 300,000 tons of steel per year and sufficient oxygen for making reducing gases to produce another 900,000 tons—a total of 1,200,000 tons of steel with the consumption of only 215,000 tons of coke. By comparison with present methods this would represent a saving per year of over 1,500,000 tons of coal together with costs of making coke and handling vast quantities of surplus materials in expensive plants to produce low-grade pig iron.

Conclusions

On account of the very low investment charges for coal-gas-making apparatus and ore reduction apparatus as described, such equipment would be adaptable to both continuous and seasonal operation. For instance, the load on a water-power and electrolytic-cell plant could be maintained at a full 100 per cent throughout the year while production could be shifted, if and as desired, from cheap gas for winter heating over wide areas to the reduction of ores at other seasons. By suitably adjusting production to requirements such advantages as the following might obtain:

1—In cities, a supply of the ideal form of fuel (low-cost gas) for domestic heating in winter and other uses the year round.

2—For rural domestic users, low-cost gas for all requirements in light and heat and for certain power demands.

3—For industries, low-cost gas and also, when needed, low-cost oxygen to elevate flame temperatures and thus further economize on fuel.

4—Development of new processes and products through the availability of high-temperature heat at low cost.

5—Reduction of ores by gases with great economy in coal and other costs.

6—Utilization of lean and inferior ores and mine wastes, such as those of the Sudbury nickel areas.

7—Processing of bituminous coal for the recovery of oils, ammonia, tars, etc., and the complete gasification of residues to produce carbon monoxide and hydrogen.

8—Low-cost water gas for synthetic production of liquids from coal.

9—Low-cost hydrogen for synthetic ammonia, coal liquefaction, ore reduction, etc.

10—Development of 100 per cent annual load factors on water-power plants.

11—"Further spread of water power"—in the sense that the gases produced contain some sixfold the total energy of water power as now actually utilized and that cheap gas is more generally useful and more cheaply and efficiently distributed than electricity.

12—Substitution of gas for anthracite, coke, bituminous coal, oil fuel, and also for certain domestic and industrial uses for electricity.

13—Permit certain regions to greatly reduce fuel importations as well as importations of steel and other metals and products.

Such possibilities as these should receive the attention of power interests and others concerned. To invite activity in these lines it should only be necessary to show that oxygen and hydrogen can find simultaneous and unlimited use and that water power used in their generation can vastly reduce importations of fuel and permit greater development of native mineral resources. In fact, it might be said that a 100,000-horsepower hydroelectric plant could be made the equivalent of a coal mine producing coal in various amounts even up to 2 million tons of coal per year for use in high-temperature industrial processes.

The study and development of only two simple operations seems to be necessary to make most of these things possible—the use of oxygen in the gasification of coal and the use of gases for ore reduction. The simplicity of the required apparatus has already been mentioned and there is no reason why such apparatus could not be used industrially within a short time.

Calendar of Meetings

American Chemical Society—75th Meeting, St. Louis, Mo., April 16 to 20, 1928.

Intersectional Meeting, Northern New York Group of Sections—Ithaca, N. Y., December 9 and 10, 1927.

Division of Organic Chemistry—Second National Symposium on Organic Chemistry, Columbus, Ohio, December 29 to 31, 1927.

American Institute of Chemical Engineers—Hotel Chase, St. Louis, Mo., December 5 to 8, 1927.

American Petroleum Institute—8th Annual Meeting, Chicago, Ill., December 6 to 8, 1927.

American Electrochemical Society—Hotel Stratfield, Bridgeport, Conn., April 26 to 28, 1928.

Conversion of Rubber into Thermoplastic Products with Properties Similar to Gutta-Percha, Balata, and Shellac[1]

I—Methods of Preparation and General Properties

By Harry L. Fisher[2]

The B. F. Goodrich Co., Akron, Ohio

THE hydrocarbon of gutta-percha has long been known to have the same empirical formula as that of the rubber hydrocarbon—namely, C_5H_8—and also the same unsaturation—one double bond for each C_5H_8 group.[3] The same is true of the balata hydrocarbon although the experimental data in this case are meager.[4] The physical properties, however, are quite different, gutta-percha and balata being thermoplastics. Many attempts have been made to convert the more abundant rubber hydrocarbon into the less abundant, though very valuable, gutta-percha and balata hydrocarbons, but none have been successful. Harries[5] describes his attempt in which he used sulfuric acid on rubber in solution, but the product was amorphous and friable. He could not obtain it ash-free, stating: "I think, however, that it has the same composition, $C_{10}H_{16}$, as rubber, but probably a higher molecular weight." That such a conversion is probable is indicated by the recent work of Staudinger,[4] who has shown that the three corresponding hydrogenated hydrocarbons are identical as judged by their refractive indices and composition. The present writer has not succeeded in making this complete change, but he has been able to convert rubber into isomeric hydrocarbons which are similar not only to gutta-percha and balata but also to shellac.[6]

By heating in sheet form a mixture of rubber with approximately 10 per cent of its weight of either an organic sulfonyl chloride or an organic sulfonic acid, for several hours at 125–35° C., the rubber is converted into tough, thermoplastic products resembling gutta-percha and hard balata. If heated similarly in bulk there is a pronounced exothermic reaction and the products formed are hard and thermoplastic like shellac. *p*-Toluenesulfonyl chloride and *p*-toluenesulfonic acid are suitable reagents. A mixture of 7.5 parts of *p*-phenolsulfonic acid and 100 parts of rubber, under similar conditions, gives a flexible product similar to gutta-percha, which is soluble in benzene, is a very good adhesive, and is the basis of the Vulcalock process. Five parts of concentrated sulfuric acid milled into 100 parts of rubber and heated as above give balata types but not the soluble shellac types.

The products have been given the general name "thermoprene," and the following suffixes are used in order to designate the different types: GP, HB, and SL.

Preparation

Concentrated sulfuric acid reacts rapidly with rubber in solution, precipitating and transforming it into a much less unsaturated, insoluble, high-melting substance.[5,7] In studying the action of sulfuric and various other acids on rubber in solution, the writer noted that chlorosulfonic acid ($HOSO_2Cl$) seemed to work even more rapidly than sulfuric acid. Thinking that this difference was due to the replacement of one OH-group with Cl, he tried to mitigate its action by using a derivative in which the other OH-group was replaced with an organic radical. *p*-Toluenesulfonyl chloride was chosen and, since it is a solid, it was milled directly into the rubber. A chemical double decomposition was expected because the reagent was no longer an acid, but stoichiometric quantities could not be used under the conditions employed, only 40 parts instead of the theoretical equivalent, 280, on 100 of rubber being milled into the rubber on the first trial. Fifty grams of rubber were used. A sample of the soft mixture was heated on a watch glass in an air oven for 1 hour (10 to 15 minutes would have been sufficient) at 105° C., and a black, shiny mass was obtained which while hot yielded to the pressure of the thumb nail and was not soft and sticky like most heated rubber batches. Upon cooling it set to a hard, brittle mass! The original rubber mix was then milled with enough rubber to reduce the proportion to 20 of the reagent to 100 of rubber and a sample heated again for the same period. There were evidences of stiffening at the end of the hour, and after having been heated in the oven overnight it became hard and very tough, although its upper surface consisted of a film of resilient rubber. This rubbery film was soon found to be characteristic, since some of the reagent distils out and it was learned that small amounts of the reagent—5 parts[8] per 100 of rubber—give a resilient product which is rubbery but "short" and non-thermoplastic. Gravity disks ($1^7/_8$ inches in diameter and $^3/_{16}$ inch thick, of the type ordinarily used for determining the specific gravity of commercial stocks) of the mix with 20 parts cured for 30 and 60 minutes at 141° C. came out black, rather hard, and so tough that they could not be broken with the fingers. They cut like a hardened balata, softened in hot water, and could then be molded. Thus was opened up a new field of thermoplastics with properties that could be varied at will from hard, brittle types resembling shellac to rather soft, very tough types resembling gutta-percha and balata.

The soft balata types and the hard shellac-like products can be made from a mix containing as low as 10 parts of the

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[1] Presented before the Division of Rubber Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927. Received October 18, 1927.

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[3] Caspari, *J. Soc. Chem. Ind.*, **24**, 1274 (1905); Harries, "Untersuchungen über die natürlichen und künstlichen Kautschukarten," p. 119 (1919).

[4] Harries, *op. cit.*, p. 124; Staudinger, *Kautschuk*, p. 8 (September, 1925).

[5] *Op. cit.*, p. 6.

[6] U. S. Patent 1,605,180 (1926); Canadian Patent 256,567 (1925).

[7] Kirchhof, *Kautschuk*, p. 1 (January, 1926). The product is generally partially oxidized. Compare also Marquis and Heim, *Bull. soc. chim.*, **13**, 862 (1913).

[8] Parts as used throughout this paper will always mean "parts per 100 of rubber."

reagent, depending on the method of heating. At temperatures around 125–45° C., in a thin sheet mold in a press, or in comparatively thin sheets in an air oven, the gutta-percha and balata types are formed. After 30 minutes' heating at 141° C. they are rubbery and resilient, in 2 hours they are balata-like inside, and in 12 hours they are hard and tough. When in bulk, however, the shellac type is formed almost entirely. It is an interesting fact, also known in ordinary vulcanization with sulfur, that during the "cure" an exothermic reaction takes place with consequent rise in temperature. In thin sheets this heat is readily dissipated, but in bulk, on account of the slow rate of heat conductance, the heat accumulates, and the internal temperature often reaches 225° C., even in comparatively small batches. A sample of the mix in a test tube quickly heated in a metal bath to the same high temperature is converted into the shellac type within a few minutes, but larger batches at the lower temperatures require several hours. The time when this exothermic reaction shows itself is quite characteristic, depending upon the concentration of the reagent, the bulk of the batch, and the temperature of the surrounding medium. For 500 grams of a batch of 10 parts heated in an oven at 135° C. this exothermic reaction becomes decidedly noticeable at 180 minutes, and for a batch of 20 parts in about half this time. A 100-part batch reacts violently even while on the mill. Also in a press, if the bulk is fairly large—for example, 2 inches thick—a goodly portion of the batch is converted into the shellac type. Gases are always formed, consisting of sulfur dioxide, hydrogen sulfide, and others of a peculiar, characteristic odor. In the larger batches, on account of the high temperature, the shellac type of material becomes very limpid during the reaction and the gases bubble out easily, leaving a fine solid product, which when cold breaks with a typical conchoidal fracture. The balata-like batches are stiffer even while hot and therefore the gases do not all escape and a honeycomb mass results. However, such a product can be milled and homogenized on a hot mill and thus be freed from bubbles.

Other organic sulfonyl chlorides react similarly such as benzene-, β-naphthalene-, *m*-nitrobenzene-sulfonyl chloride. Liquid reagents like benzenesulfonyl chloride can advantageously be added to a solution of rubber, the solvent evaporated, and the residual mix heated as usual, or, better still, the rubber is allowed to soak up the reagent for several hours in a sealed tube or autoclave and then heated. Aliphatic sulfonyl chlorides also can be used, butanesulfonyl chloride giving a satisfactory reaction. Basic nitrogen groups more or less neutralize the action of the sulfonyl chloride group. For example, acetanilide-*p*-sulfonyl chloride gives only a partial reaction. The simple sulfonyl chlorides dissolve in the rubber and sometimes form almost transparent sheets on the mill. Then, on cooling and standing the crystals "bloom" out on the surface just as sulfur does.

Organic Sulfonic Acids

At first it was thought that the organic sulfonyl chlorides reacted with the rubber hydrocarbon, giving off hydrogen chloride and forming sulfones, partially represented as follows: $CH_3C_6H_4.SO_2.C_5H_7$. Accordingly, there seemed to be no reason why the corresponding sulfonic acids should not react, forming similar sulfones and giving off water instead of hydrogen chloride. *p*-Toluenesulfonic acid was therefore milled into rubber and products apparently identical with those formed with the sulfonyl chlorides were obtained. These sulfonic acids can be milled into rubber readily and of course do not give off the sharp vapors of the sulfonyl chlorides, although some sulfur dioxide and the peculiar characteristic odor are given off. Furthermore, since they are non-volatile the reaction products are more homogeneous, there being no rubbery film on the outside of batches. These acids do not dissolve appreciably, if at all, in the rubber; nevertheless the same reaction types of products are formed under similar conditions of concentration, time, temperature, and conditions of heating. In other words, resilient, rubbery products, soft gutta-percha and hard balata types, and shellac-like products are obtained with the use of the sulfonic acids as with the sulfonyl chlorides. It is difficult to obtain the sulfonic acids anhydrous and also free from sulfuric acid, but a little water makes no special difference, and the sulfuric acid, although not necessary for the reaction, helps to give products which are tougher and less brittle than those obtained when the pure sulfonic acid is used alone. Sulfuric acid also raises the softening temperature.

As a rule when there is enough reagent present to bring about the characteristic exothermic reaction, the product formed is hard and shellac-like. But when 7.5 parts of *p*-phenolsulfonic acid are used and the batch is heated in the oven as usual, about 6 hours at 141° C., the same exothermic reaction takes place, but the result is a brown, flexible product, which is tough, millable on a cold mill, and resembles gutta-percha in many of its properties.

Early in the work it was noticed that the products showed a strong tendency to adhere tenaciously to metals, especially iron, and later the product just described was found to be unusually good as an adhesive and, in particular, for making rubber stick to iron, wood, etc. It became the basis of the Vulcalock process.[9]

Batches of 10 parts of *p*-phenolsulfonic acid and rubber, heated in bulk, give hard and tough shellac-like products, whereas when heated as $^1/_2$-inch sheets in soapstone for 48 hours at 110° C. they give the balata type.

A mix of 15 parts of *m*-nitrobenzenesulfonic acid, heated in bulk for 4 hours at 150° C., also gives a somewhat flexible shellac-like product; a mix of 10 parts gives a hard balata-like product, and a mix of 20 parts "cures up" and "breaks" on the mill.

Generally, organic sulfonic acids containing a free sulfonic group act chiefly like *p*-toluenesulfonic acid. Such, for example, are benzene-, β-naphthalene-, 2,5-dichlorobenzene-, 2-chlorotoluene-, 4-nitrochlorobenzene-2-sulfonic acid, benzene-disulfonic acid, sulfosalicylic acid, 1-naphthol-4-sulfonic acid, phenoldisulfonic acid, pyrogallolsulfonic acid, etc. Substances containing potential free sulfonic groups, such as *o*-sulfobenzoic anhydride, react similarly, but those in which the sulfonic group is more or less intramolecularly neutralized, as in sulfanilic acid, either do not react at all or only show slight activity. Of all the sulfonic acids containing basic nitrogen groups tried, including naphthionic, metanilic, sulfanilic, *o*-nitraniline-*p*-sulfonic, *p*-phenetidinesulfonic, β-naphthylaminedisulfonic, 8-hydroxyquinoline-5-sulfonic, 2,4-dihydroxyazobenzenesulfonic acid, etc., only one, 2-naphthylamine-1-sulfonic acid, showed any marked signs of a good reaction and that reaction was only about half complete. The inorganic aminosulfonic acid ($NH_2.SO_2.OH$), even in a mix of 40 parts, gave only a resilient mass.

Aliphatic derivatives such as ethylsulfonic acid and kerosene sulfonic acid react regularly.

Syntans, both the soluble and insoluble reaction products of *p*-phenolsulfonic acid and formaldehyde, give the usual hard thermoplastic products, and Twitchell's reagent, represented by cymenesulfostearic acid, gives a soft, somewhat thermoplastic product.

These products formed with the sulfonic acids, wherever tested, are only a little more than half as unsaturated chemically as the original hydrocarbon.

[9] Geer, Canadian Patent 256,797 (1925).

Sulfuric Acid

Every one brought up in a rubber factory learns very definitely one important rule—not to have a trace of any inorganic acid in a rubber mix;[10] and the writer was no exception. It therefore took some little time to break down such a psychological barrier and think of mixing sulfuric acid into rubber! Yet there seemed to be no reason why sulfuric acid should not act something like *p*-toluenesulfonic acid. Fossil flour was chosen as a carrier for the acid, and in the first experiment 5.50 grams of concentrated sulfuric acid and 2.75 grams of fossil flour were mixed into 50 grams of pale crepe on a small mill. The rubber turned red-brown, became sticky, went over on the back roll, gave off the odor of sulfur dioxide, and then suddenly stiffened and became so hard and tough that it could only be removed by means of a chisel. A mixture of 5 parts worked all right and on being heated in the oven for 3 hours at 138° C. became a hard, very tough, thermoplastic mass. In larger batches it was very difficult to complete the mixing, since a partial reaction makes the rubber tough and "short," and causes it to drop off the mill. This difficulty was overcome, however, by using diluted acid of 70 to 80 per cent concentration. Furthermore, by keeping the rubber thin on the rolls and thereby keeping down the temperature, even concentrated sulfuric acid without any carrier or without being diluted was milled in! On corrugated rolls acid to the extent of 33 parts, mixed with clay, has been milled in. These high-acid batches crumble off the mill, but some even then can be molded in a plunger mold.

The sulfuric acid batches cure up to thermoplastic, hard balata types. The temperature rise is considerable in bulk and yet none of these batches has ever been observed to go over into the shellac type of product. The reason for this is not clear. On being heated in thin sheets they can be made to become more or less brittle, depending upon the usual factors of concentration, time, and temperature. Those containing water must, of course, be heated longer than those without it. Batches of 5 parts in a sheet mold in a press give gutta-percha-like products in 3 hours at 177° C., and hard balata types in 6 hours. In bulk or in large sheets it is usually best to heat for 24 hours or longer at 110–25° C. The weight loss is in most cases, not counting any water, approximately 4 per cent. Batches of 3 parts give soft, resilient masses resembling "short," soft-vulcanized rubber, which mill very much like cured inner-tube scrap. The sulfuric acid batches while being heated give off an odor reminiscent of chicory.

In attempting to carry the sulfuric acid into the rubber in the form of an organic combination, diphenylamine sulfate was tried and found to work very well. Only salts of similar very weak bases will react. Other amine sulfates such as those of aniline, benzidine, 2,4-dimethylquinoline, and guanylurea, and also of ammonia, show no apparent action. Crystalline aluminum sulfate and ferric sulfate show a partial reaction, probably on account of the acid formed by hydrolysis. Cellulose (cotton) (4 parts) dissolved in concentrated sulfuric acid (10 parts) gives the usual reaction. Only 2 parts of sulfuric acid with 10 parts of trioxymethylene in 100 parts of rubber, when heated as usual, give a semihard rubber sponge. Dimethyl sulfate reacts like sulfuric acid.

General Notes and Observations

OTHER RUBBERS—Pale-crepe rubber was used in most of the work, but other types of raw rubber can also be used. The relative proportions of the reagents, the time, and the temperature generally have to be varied according to the rubber or its physical condition. Furthermore, the products will vary under similar treatment according to the physical condition of the original rubbers. Synthetic rubbers, such as the German methyl-rubber-W and methyl-rubber-H, undergo similar transformations, physically and chemically. Reclaimed rubbers also react, but larger proportions of reagents must be used since reclaims generally contain alkaline substances which neutralize the reagents. Products with much better properties can be obtained with reclaimed rubbers if some pale crepe is added. The organic sulfonyl chlorides react the best with reclaims.

MILL ROLLS—The reagents apparently cause no damage to the steel mill rolls, for rolls that have been used for several years have shown no noticeable deterioration. It is, of course, advisable to clean off any film of acid that may remain at the end of a day's work by means of an old piece of rubber.

WORKING AND COMPOUNDING THE PRODUCTS—Since the products are thermoplastics they can be milled on hot rolls. The shellac-like products work very much like shellac itself but have more "body" while hot. The gutta-percha- and balata-like products sometimes mill very nicely, and sometimes they are "short" and tend to "break." Usually by keeping the rolls tight even this difficulty can be overcome. The phenolsulfonic acid product (7.5 parts) can be milled on cold rolls. Compounding is done in the usual manner on the hot rolls, and alkaline ingredients can be included, if desired, in order to neutralize any acid.

Vulcanization

The products can be vulcanized by heating with sulfur, but since they are chemically less unsaturated than rubber they do not take up so much sulfur. Sulfur converts them into non-thermoplastics if the heating is long enough. In fact, even 2 parts of sulfur with long heating (about 15 hours at 141° C.) converts them into insoluble, non-thermoplastic products like hard rubber. If sulfur is milled into the original mixture along with the acid the product will be much higher softening, and if more than about 20 parts of sulfur is used the product will scarcely soften within the thermoplastic range. The action of sulfur will be discussed further in the second part of this paper.

Solubility

The solubility depends on the type of product. The gutta-percha-like product from 7.5 parts of *p*-phenolsulfonic acid can be made completely soluble in the ordinary rubber solvents, such as benzene, chloroform, carbon tetrachloride, carbon bisulfide, gasoline, turpentine, tetralin, etc. The shellac type dissolves almost completely in these same solvents, depending on how it is made and the amount of sulfuric acid used in the mixture. These solutions are much less viscous than solutions with corresponding amounts of ordinary, masticated rubber. Concentrations of 25 per cent are easily obtained. The other types are more or less soluble, but those made with sulfuric acid alone are sometimes very difficultly soluble, especially if they have had a long heating. Vulcanization with sulfur makes them all much less soluble.

General Chemical and Physical Properties

The general chemical properties are very much the same as those of the rubber from which they are derived, except that, as already mentioned, they are less unsaturated. They form addition products with hydrogen chloride, sulfur, oxygen, etc. Bromine substitutes as well as adds. They are resistant to the action of alkalies and inorganic acids, except

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[10] Goodyear, "Gum Elastic," Vol. I, p. 154 (1855); Whitby, *India Rubber J.*, **68**, 618 (1924), states: "The fact * * * that the material extractable from raw rubber by means of acetone consists largely of free acids is not without an ironical aspect, when it is recalled that the presence of any acidic material in rubber has generally been regarded with suspicion, and has often been roundly and indiscriminately declared to be harmful."

nitric acid, especially when these are dilute. The chemical properties will be discussed in greater detail in Part II of this paper.

The general physical properties have already been described. In addition, they absorb only a very small amount of water. Furthermore, the gutta-percha- and balata-like products lack the snap of the natural varieties. When freshly prepared and molded they all have a so-called surface tack, noticeable as a rule only when the fingers are warm and moist with perspiration.

A more definite idea of the physical properties of some of the products can be obtained from the accompanying table. The samples were generally homogenized on a hot mill and then molded as 6 by 8 by 1/4-inch sheets or as disks 1/4 inch in thickness and 7 inches in diameter.

Physical Properties of Products

TESTS[a]	*A*	*B*	*C*	*D*	*E*	*F*
Specific gravity (room temperature)	0.980	0.999	1.016	0.993	0.993	1.003
Tensile strength, lbs. per sq. in. (22° C.)	2600	2300	4800	4700	660	Too brittle to test
Elongation at break, per cent	27	29.8	1.3	1.7	0.6	
Impact strength, in. lbs. per sq. in. at 0° C.	50	20.8	41	42	6.6	1.4
Ultimate compressive strength, lbs. per sq. in.	5400 (21° C.)	3850	10,600 (24° C.)	8600 (32° C.)	9000 (32° C.)	7100 (26° C.)
Ultimate transverse strength, lbs. per sq. in. (21° C.)[b]	8100	4800	7200	7000	2140	1600
Cold flow, per cent (50,000 lbs. load)	38.6 (21° C.)	38.2	17.3 (24° C.)	30.4 (24° C.)	34.3 (24° C.)	22.8 (24° C.)
Dielectric strength, volts per mm.	47,500	36,500	50,000	55,200	51,800	53,200
Thickness of sheet, mm.	(0.91)		(0.94)	(1.07)	(0.76)	(0.89)
Softening temperature, ° C.	Room temperature	...	65	77	..	..

[a] The author is indebted to E. O. Dieterich for the determinations of these physical constants.

[b] Loaded to failure rapidly.

A—A gutta-percha type prepared from 100 parts of pale crepe and 7.5 parts of *p*-phenolsulfonic acid by heating 1075 grams in a 1-gallon can for 6 hours at 141° C.

B—A hard balata type prepared from 100 parts of pale crepe and 10 parts of *p*-toluenesulfonyl chloride by heating 1/2-inch sheets in a tray for 8 hours at 100–5° C. and then 8 hours at 110–5° C.

C—A hard balata type prepared from 100 parts of pale crepe, 4 parts of concentrated sulfuric acid, and 2 parts of fossil flour, by heating in bulk for 24 hours at 120–5° C. in an oven.

D—A very hard balata type prepared from 100 parts of pale crepe and 10 parts of a moist crystalline mixture consisting of approximately 63 per cent *p*-toluenesulfonic acid, 12 per cent sulfuric acid, and 25 per cent water by heating 1/2-inch sheets in soapstone for 30 hours at 110° C. and then 67 hours at 115–25° C.

E—A shellac type prepared from the same batch as *D* but heated in bulk for approximately 4 hours at 125° C. (Note the effect of the sulfuric acid as compared with *F*.)

F—Also a shellac type but prepared from 100 parts of pale crepe and 12.5 parts of β-naphthalenesulfonic acid, and heated in bulk in an oven for several hours at 145° C.

Nomenclature

Ostromislenski,[11] Kirchhof,[7] and Staudinger[12] have also noted the diminution in the chemical unsaturation of the products formed from synthetic and natural rubber in solution under the influence of acidic reagents,[13] such as zinc bromide, sulfuric acid, zinc chloride, respectively, and very properly designated the change as due to cyclic formation. The products described in this paper, according to their unsaturation, do not fall directly into the monocylic or polycyclic nomenclature, and furthermore their properties vary much more. Therefore, it has seemed best to give these new derivatives names which are descriptive and also indicative of their origin. The general name chosen to represent them is "thermoprene," signifying a thermoplastic, unsaturated hydrocarbon derived from polyprene, Weber's name for the rubber hydrocarbon. In order to differentiate between the varieties it is suggested that to the general name certain letters be added to signify the type, such as GP for gutta-percha, HB for hard balata, and SL for shellac-like—for example, thermoprene-GP, thermoprene-HB, and thermoprene-SL.

Industrial Applications

The products can be used in various operations where thermoplastics are ordinarily employed; for molded articles, particularly molded electrical and cable insulation, diaphragms, phonograph records, etc.; and for paints and adhesives, especially for causing rubber to adhere to metal and wood in connection with tank linings, chutes, ball mills, etc.

Acknowledgment

The author gratefully acknowledges his indebtedness to W. C. Geer, former vice president of The B. F. Goodrich Company, for the liberal policy under which he worked, and to the company for permission to publish this paper.

[11] *J. Russ. Phys. Chem. Soc.*, **47**, 1915 (1915); *C. A.*, **10**, 1947 (1916).

[12] *Helv. Chim. Acta*, **9**, 529 (1926).

[13] Although Ostromislenski did not mention it, there appears to be no doubt that the transformation he described was due to the presence of the zinc bromide formed during the reaction.

II—Chemistry of the Reaction

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WHEN organic sulfonyl chlorides are milled into rubber and the mixtures are heated, the rubber is converted into thermoplastic products which, according to the conditions employed, resemble gutta-percha, balata, or shellac. As mentioned in Part I, it was thought at first that the reagent reacted with the rubber hydrocarbon possibly forming sulfones; otherwise the reaction seemed very much like ordinary vulcanization since the results varied with the time and temperature and concentration of the reagent, and since even the amounts of the reagent used were comparable with those of sulfur. In fact, when compared with the customary 5 parts of sulfur (32) on 100 parts of rubber, 10 parts of *p*-toluenesulfonyl chloride (190.5) is only one-third the molecular equivalent. The idea of sulfone formation led to the use of the organic sulfonic acids, which gave even more useful products, and finally to the use of ordinary sulfuric acid itself. This theory, however, was proved to be untenable.

After a rather thorough study of the different types of reagents and the conditions under which the various products are formed, a detailed study of the chemistry of the reaction was undertaken. The jet black, shellac-like products (thermoprene-SL) were examined first, since they are almost completely soluble in benzene, carbon tetrachloride, etc., and can be handled most easily. By filtering one of these solutions a clear, yellow filtrate was obtained and by adding acetone there was precipitated a beautiful white powder which was found to contain no sulfur. Repetitions of this experiment with different preparations always gave the same results. Analyses then showed that the product was a hydrocarbon of the same composition as that of the original rubber hydrocarbon, C_5H_8. In benzene it redissolved with the same yellow color and gave no noticeable depression of the freezing point. Its molecular weight must therefore be very large. Finally, it was found that the unsaturation was 57 per cent of that of the rubber hydrocarbon.

The other types of products are much more difficult to handle and the results are not so complete as those just given, but they lead to the same conclusions. The reaction, therefore, is an isomerization in the generic sense of the term, with the probable formation of internal cyclic structures.[1]

Note—The reaction in its general aspects is so much like ordinary vulcanization with sulfur that the authors believe that their findings help to substantiate that theory of vulcanization which holds that the first and chief stage is the change in the rubber hydrocarbon to another form, designated by some writers as the "stabile" form, and that the chemical addition of sulfur is a secondary, although probably necessary, reaction to give a more useful practical product.

The shellac-like products formed by the action of organic sulfonic acids on rubber have been studied chiefly. After purification the chief constituent is found to be a hydrocarbon with the same empirical formula as that of rubber, C_5H_8, and it is 55 to 60 per cent as unsaturated as the rubber hydrocarbon. Addition products of hydrogen chloride and hydrogen bromide have been prepared. Vulcanization with sulfur gives a maximum combined-sulfur content of about 21 per cent, corresponding to 57 per cent unsaturation as compared with rubber. Oxidation, hydrogenation, bromination, nitration, etc., have also been studied. The purified hydrocarbon is white and is completely soluble in the rubber solvents and insoluble in alcohol, acetone, etc. It is much more stable toward heat than rubber. The gutta-percha and balata types are only partially soluble, but analyses, yields, etc., indicate that they consist of similar isomeric hydrocarbons.

The unsaturation of these products, as so far determined, varies from 55 to 65 per cent of that of the rubber hydrocarbon. These figures were obtained from the analyses of certain addition products and by the Kemp-Wijs[2] method using iodine-chloride. Calculations from the hydrogen chloride addition products indicate that the hydrogen chloride caused a further decrease in the unsaturation during the preparation of the addition product. The addition of sulfur and oxygen under certain conditions checks very closely the results with the Kemp-Wijs method. The products therefore are probably not identical with those recently reported by Staudinger and Widmer[3] and obtained by the action of zinc and hydrogen chloride on rubber hydrochloride, and of heat on rubber alone,[4] since the unsaturation is higher, but from a comparison of the other chemical and the physical properties there is no doubt but that they all belong to the same class.

Fate of the Reagent

The yields of products are approximately the same as the weight of the rubber used, and this fact is in accord with the theory outlined above. Part of the reagent apparently oxidizes a small amount of the rubber hydrocarbon or, as is more likely, some of the non-rubber constituents, since sulfur dioxide is always evolved. In the case of *p*-toluenesulfonic acid and of β-naphthalenesulfonic acid, toluene and naphthalene have been identified as decomposition products. Much of the reagent remains in the final product either as such or as the ammonium salt or both. The ammonia comes from the decomposition of the nitrogenous constituents in the raw rubber. Extraction with acetone or water will remove them.

Purification and Analysis

The shellac-like products always contain at least a small portion of material which swells but does not dissolve in the solvent. On this account it is best to use dilute solutions (1 to 3 per cent), and even then the filtration is often long and incomplete since the pores of the filter paper become clogged. Much better filtration and more complete recovery of the chief constituent can be had by mixing in fossil flour, using three times the weight of the substance. By further extraction of the residue it is possible to isolate and purify 85 to 90 per cent of the substance as the hydrocarbon. About 5 per cent remains insoluble in the solvent generally used, carbon tetrachloride. The clear, yellow filtrate is allowed to drip slowly into thirty times its volume of acetone, which is stirred mechanically. Beautiful white flocks are formed, which are allowed to settle, washed two or three times by decantation, and then filtered with suction.

If the original reagent was a mixture containing some sulfuric acid,[5] the flocculation takes place readily and the product is a fine white powder which is easily handled. If a very pure sulfonic acid or if a sulfonyl chloride is used, then it is necessary to add a little dilute hydrochloric or sulfuric acid to the acetone in order to cause flocculation. Cooled solutions must be used when the product is low-softening; otherwise it will form a mass which occludes solvent and other impurities. For analytical purposes the precipitates were redissolved, filtered, precipitated two to four times, and finally dried *in vacuo* over concentrated sulfuric acid.

The results of analyses of two representative shellac-like products (thermoprene-SL) prepared from a typical mixture of *p*-toluenesulfonic acid and sulfuric acid, are as follows:

	CARBON %	HYDROGEN %	TOTAL %
Found (1)	87.95	11.93	99.88
	87.93	11.76	99.69
(2)	87.95	11.76	99.71
	88.20	11.63	99.83
Calcd. for C_5H_8	88.16	11.84	100.00

Chemical unsaturation as compared with rubber hydrocarbon, by Kemp-Wijs method: 57.00, 57.31 per cent.

A complete analysis of a similar product prepared as a 1000-pound batch, pulverized, but only washed and oven-dried, is as follows:

	CARBON %	HYDROGEN %	SULFUR %	ASH %	MOISTURE %	OTHER IMPURITIES INCLUDING OXYGEN[a] %	TOTAL %
Found	85.67	11.46	0.95	0.87	0.53		
	85.62	11.39	0.95	0.83			
Av.	85.65	11.43	0.95	0.85	0.53	0.59	100.00
Calcd. on basis free from sulfur, ash, moisture, and other impurities, including oxygen:	88.22	11.77					99.99
Calcd. for C_5H_8:	88.16	11.84					100.00

Chemical unsaturation as compared with rubber hydrocarbon, by Kemp-Wijs method: 57.00, 57.39 per cent.

[a] By difference.

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[1] See Part I, under "Nomenclature."

[2] Kemp, THIS JOURNAL, 19, 531 (1927).

[3] *Helv. Chim. Acta*, 9, 529 (1926).

[4] Staudinger and Geiger, *Ibid.*, 9, 549 (1926); Fisher and Gray, THIS JOURNAL, 18, 414 (1926).

The purification of the shellac-like products prepared with p-toluenesulfonyl chloride gave some difficulty. Chlorine was always found in the purified products. This, however, was due not to chlorination, but to the carbon tetrachloride which could not be removed completely from the samples. A hydrocarbon solvent was not used because no trace of it could then be had and the carbon and hydrogen determination would be much further off.

	CARBON	HYDROGEN	TOTAL C AND H	CHLORINE	GRAND TOTAL
	%	%	%	%	%
(1) Ordinary purification	86.53	11.67	98.20	1.70	99.90
	86.41	11.51	97.92	1.71	99.63
Ratio C:H, 5:7.97					
(2) Very thorough purification, three precipitations, using dilute H_2SO_4 for flocculation	87.38	11.85	99.23		
	87.27	11.63	98.90		
Ratio C:H, 5:8.07					
(3) Same, after having been heated for 90 hours at 150° C. *in vacuo*	87.21	11.86	99.07		
	87.38	11.74	99.12		
Ratio C:H, 5:8.04					
Calcd. for C_5H_8	88.16	11.84			

The original product contained even less chlorine:

	CHLORINE *Per cent*	
Added as reagent in original mixture (calcd.)	1.69	
Found:		
In product	0.45	0.49
After acetone extraction	0.25	0.19

The gutta-percha-like product (thermoprene-GP) from 7.5 parts of p-phenolsulfonic acid is somewhat soft at ordinary temperatures and gave much trouble in the purification. Even after having been three times dissolved and precipitated, and the solvent slowly removed under diminished pressure in a stream of nitrogen, on the steam bath, the removal was not complete.

	CARBON	HYDROGEN	TOTAL
	%	%	%
Found	84.20	11.13	95.33
Calcd. for C_5H_8	88.16	11.84	
Ratio C:H, 5:7.93			

A sample from a larger lot of thermoprene-GP which had only been washed on a mill and dried in an oven gave the following results:

	CARBON	HYDROGEN	SULFUR	ASH	MOISTURE	OTHER IMPURITIES INCLUDING OXYGEN[a]	TOTAL
	%	%	%	%	%	%	%
Found	86.15	11.57	0.50	0.27	0.23		
	86.73	11.63	0.47				
Av.	86.44	11.60	0.49	0.27	0.23	0.97	100.00
Calcd. on basis free from sulfur, ash, moisture and other impurities, including oxygen:							
	88.16	11.83					99.99
Calcd. for C_5H_8:							
	88.16	11.84					100.00

Chemical unsaturation, as compared with the rubber hydrocarbon, by the Kemp-Wijs method, 65.56 per cent.

[a] By difference.

A hard balata type (thermoprene-HB) was prepared from 1000 grams of deproteinized rubber (prepared by steaming a rubber mixture containing sodium oleate and sodium carbonate), 50 grams of concentrated sulfuric acid, and 17 grams of fossil flour, heated in a 1-gallon can in the oven for 6 hours at 149° C. This gave a greater proportion of soluble material than when pale crepe itself was used. A portion was extracted with boiling tetrachloroethane and precipitated twice, yielding 53.8 per cent of the original. It contained no sulfur and no nitrogen. The final sample was reddish brown.

	CARBON	HYDROGEN	TOTAL	RATIO C:H
	%	%	%	
Found	82.55	10.75	93.30	5:7.81
	81.99	10.87	92.86	5:7.93
Calcd. for C_5H_8	88.16	11.84	100.00	

The difference from the theoretical in this case may be due to oxygen, since the sulfuric acid mixtures always give off more sulfur dioxide than those with the other reagents. The portion insoluble in the tetrachloroethane analyzed as follows:

	CARBON	HYDROGEN	ASH	TOTAL	RATIO C:H
	%	%	%	%	
Found	75.20	9.95	6.56	91.71	5:7.94

German synthetic methyl-rubber-W (warm polymerization product of 2,3-dimethylbutadiene-1,3), in the thermoprene-SL recipe, gave a flexible, shellac-like product which, upon being purified in the regular way and analyzed, gave the following:

	CARBON	HYDROGEN	TOTAL
	%	%	%
Found	87.63	12.17	99.80
Calcd. for C_6H_{10}	87.72	12.28	100.00

The purified thermoprenes-SL are soluble, giving clear, yellow solutions in benzene, p-cymene, gasoline, chloroform, carbon tetrachloride, carbon bisulfide, turpentine, tetralin, decalin, and molten camphor. They swell a little in ether, aniline, and amyl acetate, and are insoluble in methanol and ethyl alcohol, acetone, and glacial acetic acid. Their behavior in the melting point determination varies somewhat with the method of preparation. Generally they soften at 100–5° C., slowly melt at 110–30° C., and at 130–5° C. become amber-colored droplets clinging to the walls of the tube. They are optically inactive. Thin films formed for the determination of the refractive index in the Abbé refractometer were too delicate to be used.

Action of Sulfur

Under the influence of heat sulfur adds chemically to the thermoprenes, converting them eventually into insoluble, hard non-thermoplastics. This change to a non-thermoplastic, like the vulcanization of rubber, can be made by as low as 2 per cent of sulfur, provided the time is extended to 15–20 hours at 141° C., as already mentioned in Part I. However, if they are saturated with sulfur in solution they remain soluble and thermoplastic.

A mixture of 100 parts of the washed and dried thermoprene-SL and 67 parts of sulfur was made on the hot mill. (Only 47 parts of sulfur are required theoretically to saturate the rubber hydrocarbon.) Two samples were heated in an oven at 134–6° C., one (*A*) for 9 hours and the other (*B*) for 17 hours. Both were then ground to 60-mesh and extracted with acetone for two full days and nights. *A* lost 20.71 per cent and *B*, 21.60 per cent by weight. The extracted samples were dried and analyzed for sulfur:

	SAMPLE *A*			SAMPLE *B*	
	Sulfur	Less 0.95% S in original		Sulfur	Less 0.95% S in original
	%	%		%	%
	22.33			22.74	
	22.24			22.72	
Av.	22.29	21.34	Av.	22.73	21.78

Completely sulfurized rubber $(C_5H_8S)_x$ contains 32.01 per cent sulfur. Since the percentage of sulfur is not a linear function of the amount of unsaturation as compared with the rubber hydrocarbon, in order to determine the percentage of unsaturation from the combined sulfur it is convenient to construct a curve from the theoretical amounts of sulfur combined assuming different per cents of unsaturation. For example, C_5H_8S containing 32.01 per cent

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[5] Much of the early work was done with p-toluenesulfonic acid prepared according to Lange, D. R. P. 57,391 (1891). This product is a crystalline mixture consisting of approximately 63 per cent of p-toluenesulfonic acid, 12 per cent of sulfuric acid, and 25 per cent of water.

sulfur would be 100 per cent unsaturation—that is, one double bond for each C_5H_8 group; $C_{10}H_{16}S$ containing 19.06 per cent sulfur would represent 50 per cent unsaturation; $C_{15}H_{24}S$ containing 13.36 per cent sulfur would represent 33.33 per cent unsaturation; $C_{20}H_{32}S$, 10.53 per cent sulfur, 25 per cent unsaturation; $C_{25}H_{40}S$, 8.61 per cent sulfur, 20 per cent unsaturation, etc. By means of such calculations and the curve drawn from them, it is possible to read off the unsaturation corresponding to a given percentage of sulfur. In this way it can be shown that

> *A* containing 21.34 per cent S represents 57.5 per cent unsaturation and *B* containing 21.78 per cent S represents 59.0 per cent unsaturation.

These results correspond very satisfactorily with the figures found by means of the Kemp-Wijs method—namely, 57.00 and 57.39 per cent—and it is possible, to be sure, that some substitution took place in the long heating, especially with sample *B*. These products are non-thermoplastic, but by heating at 270° C. they can be made thermoplastic again.

The experiments in solution were carried out with the purified thermoprene-SL (from *p*-toluenesulfonic-sulfuric acid mixes) in 100 cc. of *p*-cymene with a large excess of sulfur, and heated in an oil bath for the times and at the temperatures given in Table I. After the solution had thoroughly cooled the crystals of sulfur were filtered off and the filtrate was slowly added to a large volume of acetone. Mineral acids had to be used to cause flocculation except in *F*. The yields were sometimes low, even lower than can be accounted for by ordinary losses due to experimental procedure. Part of the product apparently was soluble in the acetone; and this was very noticeable in *D*, where the highest temperature was used, the product coming out as a varnish which was purified further by reprecipitation, then forming a dark yellow powder. The higher temperature in this case may have caused a change in the unsaturation. The influence of time and temperature on the amount of sulfur combined is very definite. Some hydrogen sulfide was always evolved and probably came chiefly, if not wholly, from the cymene, since sulfur and cymene alone under similar conditions gave off hydrogen sulfide.

Table I—Sulfur Experiments in Solution

Expt.	Substance	Sulfur Used	Temperature	Time	Yield	Sulfur	Unsaturation (Calcd.)
	Grams	*Grams*	*° C.*	*Hours*	*Grams*	%	%
C	2.0	10.0	170–84	3	1.45	21.15 21.08	57.0
D	1.5	7.5	185–90	3	0.85	17.16 16.47	43.5
E	1.5	7.5	128–36	7	1.40	4.46 4.21	10.3
F	1.7	8.5	87	9 × 24	1.46	1.91 1.89	4.5

Sulfur Chloride

An excess of sulfur chloride usually causes no gel formation until after the mixture has stood for 2 or 3 days, and even then it is not like the familiar vulcanized-rubber gels. The products that can be isolated by precipitation with acetone are non-thermoplastic powders.

Seventy cubic centimeters of a 3 per cent carbon tetrachloride solution of the purified thermoprene-SL were treated with 5 cc. of sulfur chloride in 20 cc. of the same solvent, and after standing a day the product was isolated by precipitation in the usual manner. Similarly, 2 grams of the purified thermoprene-SL in 100 cc. of benzene were treated with 10 grams of sulfur chloride. The solution was turbid at first but after remaining stoppered overnight it became clear and more limpid. Three days later it was precipitated in 4.5 liters of acetone. The yield was 2.51 grams. The analytical results were irregular.

	Sulfur	Chlorine[a]
	%	%
Found:		
CCl_4 solution	16.05 16.00	10.61 10.52
C_6H_6 solution	17.43 17.35	12.13 12.09
Calcd. for $C_{10}H_{16}SCl$	15.72	17.44

[a] Staudinger and Widmer[3] report that in their polycyclo-rubber-sulfur chloride product the chlorine found was only 5.62 per cent. That rubber-sulfur chloride generally shows low chlorine may be due not only to the loss of chlorine as HCl but also to the change in unsaturation of the rubber hydrocarbon by the action of the reagent.

Hydrogen Halides

Early in the work it was expected that the addition products of the hydrogen halides would give the best measure of the unsaturation, but the results varied considerably, possibly because the unsaturation was changed by the action of the hydrogen halides themselves.

Hydrogen Chloride—The purified chief constituent of thermoprene-SL was used and treated as outlined in Table II. In the first three experiments the substance used, as found out later, was slightly oxidized. The products were isolated in the usual way by precipitation in acetone, and in the first four cases it was necessary to cause flocculation by the use of hydrochloric acid. The products of Nos. 4 and 5 were non-thermoplastic.

Table II—Addition of Hydrogen Chloride

Expt.	Substance	Yield	Chlorine	Unsaturation[a]	Method of Preparation
	Grams	*Grams*	%	%	
1	2.0	2.25	2.65 2.59	5.0	3 hours treatment with dry HCl in 100 cc. CCl_4
2	2.0	1.66	12.37 12.06	26.5	4 hours in 100 cc. C_6H_6
3	2.0	1.64	15.42 15.33	34.5	6 hours in 100 cc. C_6H_6
4	2.0	1.98	8.20 8.16	16.25	3 hours in 100 cc. C_6H_6
5	1.75	1.28[b]	10.17 10.14	21.0	13 days in 100 cc. C_6H_6
6	2.0	1.75	2.18 2.12	4.0	1 day treatment with concd. HCl in 100 cc. CCl_4 on shaking machine

[a] The calculations for the curve for the hydrogen chloride addition product are:

Chlorine	Unsaturation
%	%
33.91	100.0
20.54	50.0
14.73	33.3
11.48	25.0

For the hydrogen bromide addition product the calculations are:

Bromine	Unsaturation
%	%
53.64	100.0
36.81	50.0
28.02	33.3
22.62	25.0

[b] Part lost by accident.

Hydrogen Bromide—1.5 grams of the purified thermoprene-SL were dissolved in 100 cc. of ethylene dibromide and 30 cc. of chloroform (the substance would not all dissolve in the ethylene dibromide alone) and dry hydrogen bromide was passed through the solution for 7 hours. The following day it was precipitated in 3 liters of acetone. The yield was 1.89 grams, consisting of a cream-colored non-thermoplastic product. It was dried over solid potassium hydroxide and concentrated sulfuric acid.

> Bromine found, 26.63, 26.54 per cent; which from the curve (Table II, *a*) is equivalent to 30.5 per cent unsaturation.

Halogens

Thermoprene-SL can be halogenated but, as with rubber, there is substitution, even with bromine. The products are non-thermoplastic.

Bromine—Bromine does not give a good measure of the unsaturation because there is so much substitution, and the bromine titration method[6] for unsaturation as adapted to rubber gave such irregular results that it could not be used.

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[6] Lewis and McAdams, This Journal, **12**, 673 (1920); Fisher, Gray, and Merling, *Ibid.*, **13**, 1031 (1921).

(1) Two samples of purified chief constituent, which was later found by combustion to contain 5.5 per cent of oxygen, were very slowly treated in carbon tetrachloride solution with a large excess of bromine in the same solvent, at approximately 0° C. Much hydrogen bromide was evolved, and a small amount of a precipitate formed in each case. After filtration and precipitation in a large volume of acetone, the analyses showed unexpectedly concordant results: (*A*) bromine found, 67.34, 67.15 per cent; (*B*) bromine found, 67.36, 67.50 per cent. These amounts of bromine are close to that in rubber bromide, 70.13 per cent, and are much greater than those obtained with the very pure starting material. Whether they hold any significance we do not know.

(2) Two grams of very pure chief constituent in 150 cc. of redistilled carbon tetrachloride were cooled to 0° C., and 3 cc. of bromine in 50 cc. of carbon tetrachloride added during 40 minutes with good stirring. Considerable hydrogen bromide was formed, but no jelly particles separated out. It was then precipitated in 3.5 liters of acetone, filtered, washed by decantation, etc., and dried over solid potassium hydroxide and concentrated sulfuric acid. The product was cream-colored; yield, 3.62 grams. Bromine, 49.37, 49.06 per cent, indicating 41 per cent unsaturation (using a curve as mentioned under sulfur above), on the assumption that there was no substitution. Since there was substitution this figure must be a maximum.

(3) Repetition of (2). The yield was 3.55 grams. Bromine, 51.75, 51.36 per cent, indicating a maximum unsaturation of 45 per cent.

(4) Repetition of (2), but the reaction mixture was allowed to stand in the refrigerator overnight before purifying. Yield, 4.07 grams. Bromine, 57.20, 56.67 per cent, indicating a maximum of 57.3 per cent unsaturation. This figure corresponds closely with the best ones for unsaturation, but is probably fortuitous. It is of interest to note that the yield in this case is 60.7 per cent of the theoretical if we assume 100 per cent unsaturation; that is, $C_5H_8Br_2$ is formed.

IODINE—Only one experiment was carried out with iodine. One gram of the chief constituent in 50 cc. of carbon tetrachloride was treated with 4 grams of iodine in the same solvent. No hydrogen iodide was noticed. After 2 days it was purified as usual, and it was necessary to use mineral acids to cause flocculation. The yield of a greenish powder was 0.9 gram. Iodine found, 16.37, 16.01 per cent, which, from the curve prepared as with bromine, etc., is equivalent to only 5.5 per cent unsaturation. (This is about the figure obtained for unsaturation by means of the bromine titration.)

Oxidation

AIR—A sample of thermoprene-SL on a watch glass in an air oven at 130° C. gained in weight 3.2 per cent in 71 hours, 5.06 per cent in 304 hours, and 5.63 per cent in 445 hours.

Table III—Air Oxidation at Room Temperature

TIME	INCREASE IN WEIGHT: In cabinet (0.2235 g.)	INCREASE IN WEIGHT: In desiccator (0.2935 g.)	TIME	INCREASE IN WEIGHT: In cabinet (0.2235 g.)	INCREASE IN WEIGHT: In desiccator (0.2935 g.)
Days	%	%	*Days*	%	%
2	0.95	0.14	107	12.48	13.18
7	1.92	..	138	14.94	15.50
11	3.24	..	168	16.24	16.63
18	4.43	0.75	204	17.63	17.88
25	5.86	1.64	291	19.86	18.61
32	6.26	2.45	361	26.44	20.14
39	7.56	3.07	898	34.45 (?)	23.51
46	7.86	3.71	1080	30.02	22.97 (?)
57	9.53	4.84	1261	31.72	23.85
89	11.23	9.64			

In order to determine the air oxidation at room temperature two samples of the chief constituent were allowed to remain on watch glasses—one in a cloth-covered cabinet where it would be free from dust but not from moisture, and the other in a desiccator over concentrated sulfuric acid. The powders were white in the beginning but finally became deep yellow, whereas another sample sealed in nitrogen did not change at all. The theoretical weight increase to form $(C_5H_8O)_x$ is 23.54 per cent. From Table III it is seen that the sample in the presence of moist air went beyond this amount during the time of this experiment, but the one in dry air just reached it and has remained approximately there, not increasing appreciably at the present writing.

A sample that had been dissolved in carbon tetrachloride and had stood for 3 months in a cork-stoppered flask was precipitated with acetone and purified in the usual manner. Upon analysis it was found to have been somewhat oxidized. It contained no ash.

	CARBON	HYDROGEN	TOTAL	OXYGEN (by diff.)
	%	%	%	%
Found	83.09	11.04	94.13	5.87
	83.15	11.02	94.17	5.83

Another sample that had been in gasoline solution in a cork-stoppered, wide-mouth bottle for the same period of 3 months separated out as a tough gel. This gel was removed, broken up, purified by extraction with carbon tetrachloride, and finally dried and analyzed. It was a yellow powder which was non-tribo-electric, showed no surface tack, and was less thermoplastic than the original. It was ash-free. The analysis indicates 55.24 per cent unsaturation in the original sample, which amount is approximately the same as that found from the addition of sulfur and by the Kemp-Wijs method.

	CARBON	HYDROGEN	TOTAL	OXYGEN (by diff.)
	%	%	%	%
Found	78.00	10.19	88.19	11.81
	78.37	10.35	88.72	11.28
	78.30	10.30	88.60	11.40
Calcd. for $C_{10}H_{16}O$	78.89	10.60	89.49	10.51

PERBENZOIC ACID—It was expected that a titration method for showing the relative unsaturation could be developed with the use of perbenzoic acid, but although some interesting results were obtained in general they varied with the concentration of the reagent and also were irregular and inconsistent. A sample of pure thermoprene-SL was in contact with an excess of perbenzoic acid in chloroform solution for 21 days. It was then precipitated as a white powder with ether—it was soluble in acetone. Analysis indicated it to be $(C_5H_8O)_x$.[7]

	CARBON	HYDROGEN	TOTAL	OXYGEN (by diff.)
	%	%	%	%
Found	71.46	9.41	80.87	19.13
	71.11	9.40	80.51	19.49
Calcd. for $(C_5H_8O)_x$	71.38	9.59	80.97	19.03

A sample of powdered thermoprene-SL (0.6625 gram) was treated similarly for 24 days and the product precipitated with ligroin. Part of it was soluble in carbon tetrachloride and the remainder in chloroform. Both were purified further by re-precipitations. The first had not reached the C_5H_8O stage, and the second had gone beyond it.

PORTION SOLUBLE IN:	YIELD	FOUND: C	FOUND: H
	%	%	%
CCl_4	47.4	74.81	9.52
		75.01	9.52
$CHCl_3$	29.4	71.81	7.90
Total	76.8		

OZONE—This formed a soft, yellow, insoluble product, which upon being boiled with water gave no levulinic aldehyde, and in fact was very stable, not behaving at all like an ozonide. Staudinger and Widmer[3] had a similar experience with "polycyclo-rubber."

POTASSIUM PERMANGANATE—2.75 grams of the chief constituent in 150 cc. of carbon tetrachloride and 5 grams of potassium permanganate in 125 cc. of water were shaken for 10 days. Upon purification and precipitation with acetone, it was necessary to use dilute sulfuric acid to cause flocculation. The yield of a white powder was low, 0.93

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[7] Compare the formation of rubber oxide $(C_5H_8O)_x$, by Pummerer and Burkhard, *Ber.*, **55**, 3462 (1923).

gram. Analysis showed that it contained 2.14 per cent of ash and about 5 per cent of oxygen. The oxidation is evidently incomplete. ($C_{20}H_{32}O$ contains 5.6 per cent oxygen.)

Hydrogen Peroxide—A sample of pure thermoprene-SL treated for 14 days with 3 per cent hydrogen peroxide was shown by titration of the unused reagent to have added 5.4 per cent of its weight as oxygen.

Hydrogenation

Two attempts to hydrogenate the chief constituent in pure ligroin by using hydrogen under 40 pounds pressure at the ordinary temperature and in the presence of reduced platinum oxide[8] were unsuccessful. There was no diminution in pressure after 6 hours in one case and after 15 hours in the other, even though four times as much catalyst was used in the second case. The same conditions caused the reduction of amylene and of rubber. Staudinger and Widmer[3] were also unable to hydrogenate their polycyclo-rubber at the ordinary temperature, although they did obtain a partial hydrogenation at 270° C. and 50 atmospheres pressure.

Attempts to depolymerize or disaggregate the products by heating in a stream of nitrogen for 6 hours at 330° C. and in a sealed tube for $17^1/_2$ hours at 320° C., and then hydrogenating at room temperature, gave not over 5 per cent reduction. It was not ascertained whether the reduced product was from the original or from decomposition products.

Nitric Acid

The method developed by the senior author for nitrating rubber in solution[9] was used for nitrating the purified thermoprene-SL.

Note—The laboratory procedure is as follows: Five grams of pale crepe dissolved in 100 cc. of carbon tetrachloride are treated with 5.5 cc. of concentrated nitric acid in a glass-stoppered bottle, and the mixture is shaken mechanically for 2 or 3 days. The yellow ochre masses are filtered off with suction, washed with water, and after drying ground to a paste with water, washed, filtered, and allowed to dry. From 5 grams of acetone-extracted rubber 8.27 grams of air-dried product are obtained. The theoretical yield for a nitro-rubber, $C_5H_7NO_2$, is 8.31 grams. The bright yellow product is slightly hygroscopic; it is soluble in acetone, aniline, pyridine, acetic anhydride, nitrobenzene, and aqueous sodium hydroxide, giving a deep maroon color in the latter. The unsaturation, determined on a 1 per cent nitrobenzene solution by the Kemp-Wijs method, was 24.8 per cent of the unsaturation of a nitro-rubber hydrocarbon. It is very probable that the nitric acid has caused the change in unsaturation just as the other acids do. The product therefore is probably a nitro-polycyclo-rubber. The substance is unstable toward heat and is difficult to analyze. Found: N = 12.01 per cent, calcd. N = 12.38 per cent (but this result has not yet been duplicated). This work will be published more completely later.

On the assumption that a substance with the composition $C_5H_7NO_2$ was formed, the yield was practically quantitative. The product is a yellow amorphous powder, only partially soluble in acetone, and turns red-brown without dissolving very much in aqueous alkalies. It is much more stable when heated than the corresponding nitrated rubber. In a melting point tube it darkened at 168° C., became red-brown at about 200° C., but was not completely melted at 260° C. As with nitrated rubber the analytical results were not entirely satisfactory. Nitrated thermoprene-GP was non-thermoplastic, but completely soluble in aqueous alkali with the characteristic deep maroon color.

Heat

Thermoprene-SL is more stable toward heat than rubber, the decomposition into volatile products being practically none under 350° C. Staudinger and Widmer[3] found it necessary to heat to 350–450° C. to obtain any decomposition of their polycyclo-rubber. Carbon tetrachloride solutions of the heated thermoprenes when poured into acetone gave no precipitates, and the addition of mineral acids caused no flocculation although gummy materials finally did settle out.

Action of Other Reagents on Rubber

In order to determine whether the reagents already mentioned are the only ones that produce these changes in rubber, many other types of substances were milled into rubber and the mixtures heated similarly—that is, 15 to 20 hours at 125–45° C. None of them, however, gave products like those described above. It is of interest to note that selenic and benzeneselenonic acids showed a slight "vulcanizing" action, but phosphoric and arsenic acids, and organic phosphonic, arsonic, and siliconic acids gave only soft sticky masses. In the list that follows the figures in parentheses refer to the concentration of the reagent if other than 10 parts to 100 of rubber:

p-Toluene sulfinyl chloride gave a black, stiff, non-thermoplastic, rubbery mass; *p*-toluenesulfinic acid gave a black, resilient product; tetrachloroquinone (chloranil) (20) gave a product like "short," soft-vulcanized rubber; picryl chloride (20), a product which was black, shiny, and like overvulcanized rubber; *p*-tolylmercuric chloride (30) gave a soft sticky product, and mercury-*p*-ditolyl (30), heated 48 hours at 148° C., gave a resilient mass; selenic acid (6 and 15) gave rubbery products; benzene selenonic acid (20) acted similarly, but selenious acid made no apparent change.

Concentrated hydrochloric acid (30) mixed with fossil flour, heated 20 hours at 175° C., gave a soft-vulcanized product.

Phosphoric acid, sirupy, even up to 20 parts with fossil flour, and heated 6 hours at 200° C., gave only soft, sticky masses. Similarly with arsenic acid, and the organic phosphonic, arsonic and siliconic acids, such as *p*-toluenephosphonic, α-phenyl-β-benzoylethylphosphonic acid, *p*-toluenearsonic, *p*-phenolarsonic, *p*-nitrophenolarsonic, arsanilic (40), and toluenesiliconic acid.

The following gave only soft, sticky masses: *p*-toluene sulfonamide (40), diphenyl sulfone (20), di-(*p*-hydroxyphenyl)-sulfone (20), sulfonal, phenyl *p*-toluene sulfonate, *o*-benzoic sulfinide (saccharin) (20), sodium salts of several simple sulfonic acids, 1,8-naphthyl sultone, oxalic acid, phenol (40), tribromophenol (40), α- and β-naphthol (40), nitroso-β-naphthol, trioxymethylene (40), trioxymethylene (15, mixed with aniline sulfate, 2), phthalic anhydride (30), hexamethylenetetramine (40), methylene-amino-aceto-nitrile (40), *p*-nitrobenzoyl chloride, diphenylcarbamide chloride, acetone sodium bisulfite, sodium bisulfite, potassium bisulfite (50), potassium bisulfate (40), sodium ferrocyanide (40), cupric sulfate, cryst. (40), nickel sulfate (40), gypsum (50), uranium acetate (40), chromic anhydride (20), stannic oxide (20), molybdic acid (20), vanadic acid (20), titanic acid (20), and tungstic acid.

Acknowledgment

The authors extend their thanks to W. C. Geer, former vice president of The B. F. Goodrich Company, for the liberal policy under which they were allowed to work, to E. J. Scharch for analytical assistance in the sulfur and halogen determinations, to A. E. Gray for the Kemp-Wijs determinations, and to the Goodrich Company for permission to publish the results.

Part III

Methods of converting rubber in solution into similar thermo-plastic and non-thermoplastic isomers will be given in a later paper.

Carbolic Acid Duty Reduced—President Coolidge has issued a proclamation decreasing the duty on phenol from 40 per cent ad valorem upon the basis of the American selling price as defined in the Tariff Act, and 7 cents per pound, to 20 per cent ad valorem and $3^1/_2$ cents per pound. This reduction of 50 per cent of the present duty is the maximum reduction permissible under the Tariff Act.

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[8] Adams, *et al.*, *J. Am. Chem. Soc.*, **44**, 1397 (1922); **45**, 1071, 2171 (1923).

[9] U. S. Patent, 1,609,806 (1926).

Preparation of Pyrrole[1]

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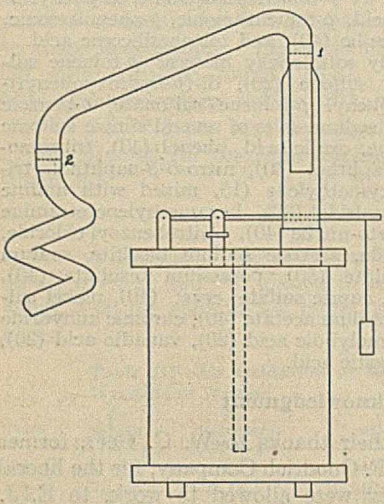
During the last few years several methods have been proposed for the manufacture of pyrrole. Michelman[2] suggested that this substance could be obtained on a large scale by the destructive distillation of scrap leather. The value of this method remains uncertain, however, since the yield of pyrrole obtainable is not given and the separation of the pyrrole from the great variety of other products which must be formed would involve considerable labor. Tschitschibabin[3] has shown that pyrrole and other compounds are obtained when acetylene and ammonia are heated in the presence of a suitable catalyst, and it has been proposed to manufacture pyrrole by this process.[4] Because of the small amounts of pyrrole present in coal tar and in bone oil and the labor incidental to the isolation of the compound, the manufacture of pyrrole from these sources is hardly practical.

Although pyrrole at present finds little, if any, use in the laboratory or in the chemical industries, and the present high cost of the material in this country precludes any prospective use, it is quite possible that pyrrole, or products prepared from it, would find extensive application if it could be obtained cheaply and in large quantities. It is well known that the substituted tetrahydropyrrole nucleus is found in nicotine, atropine, cocaine, hemoglobin, and chlorophyll. If a more suitable hydrogenation process for pyrrole and its derivatives than any known at present could be discovered, many important synthetics in the field of insecticides, synthetic drugs, and products of biological importance might possibly be obtained from pyrrole itself instead of by the more or less complex syntheses from aliphatic nitrogen compounds.



Apparatus for Preparation of Pyrrole Large-Scale Experiments

Several investigators have shown that ammonium mucate yields pyrrole when heated, and since mucic acid is now a cheap article of commerce,[5] the writers began an investigation to determine whether or not the preparation of pyrrole from ammonium mucate would be practicable on a large scale.

Schwanert[6] heated dry ammonium mucate, but Goldschmidt[7] found that addition of glycerol to the dry salt was advantageous. More recently Khotinsky[8] modified the procedure in that he heated ammonium mucate and glycerol in a stream of ammonia. No yields are given except by Khotinsky, who studied the reaction only with small amounts of ammonium mucate. He found, for example, that the ammonium salt prepared from 50 grams of the acid yielded 6.7 grams of pyrrole, which corresponds to 41 per cent of the calculated amount.

Preparation of Ammonium Mucate

The writers prepared ammonium mucate by adding mucic acid to an excess of ammonia water (three and one-half times that required theoretically) of a technical grade, thoroughly stirring the mixture for some time. Under these conditions the ammonium salt is formed in an extremely finely divided state, and filtration is a troublesome task. If the mixture is heated for a short period, or allowed to stand for about 10 days, the salt becomes granular and can be filtered readily. Only a small amount of the ammonium salt remains dissolved in the filtrate. According to Johnson,[9] ammonia is evolved when a solution of the diammonium salt of mucic acid is concentrated and the acid ammonium salt is formed.

The air-dried material was reduced to a fine powder. In several instances analyses showed that the ammonium mucate contained about 3 per cent of water and that the amount of ammonia which could be liberated by the action of concentrated sodium hydroxide varied from 12.9 to 13.9 per cent (calculated 14.0 per cent).

Preparation of Pyrrole

Small-Scale Experiments—One hundred grams of ammonium mucate were thoroughly mixed with 80 cc. of glycerol which had been heated previously to about 100° C. The mixture was put into a liter round-bottom flask, the neck of which was attached to a 6-inch (15-cm.), one-bulb distillation column, which in turn was connected to a Liebig condenser. The flask was buried to the neck in sand and heated with a Méker burner. After 20 minutes a mixture of water, pyrrole, and ammonium carbonate began to collect in the receiver. Two to three hours were usually required to complete the process. The upper layer of the distillate, which consisted of quite pure pyrrole, was separated and dried with solid sodium hydroxide. The pyrrole was then purified by distillation. The yield of pure material varied from 40 to 52 per cent of the calculated amount.

Khotinsky saturated the glycerol with ammonia, and in some cases passed a stream of ammonia through the apparatus during the reaction. The writers found, however, that better yields of pyrrole could be obtained without the use of this gas, as the presence of excess ammonia caused the reaction mixture to foam, in a manner which could not be controlled, as soon as pyrrole began to form.

Large-Scale Experiments—After fairly consistent yields of pyrrole had been obtained on a small scale, the apparatus shown in the accompanying figure was designed for the preparation of larger quantities.

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[1] Received July 25, 1927.

[2] This Journal, 17, 247, 471 (1925).

[3] *J. Russ. Phys.-Chem. Soc.*, 47, 703 (1915); *C. A.* 9, 2512 (1915).

[4] Chemische Fabrik Rhenania Akt.-Ges., Stuer and Grop, British Patent 147,067; *C. A.* 14, 3673 (1920); Brutzkus, British Patent 155,776; *C. A.* 15, 1585 (1921).

[5] A very pure grade of mucic acid (99.7 per cent pure), prepared by the improved LaMotte process, is sold by the Montana Products Co., Eureka, Mont., for 28 cents a pound in large lots.

[6] *Ann.*, 116, 270, 278 (1860).

[7] *Z. Chem.*, Neue Folge, 3, 280 (1867).

[8] *Ber.*, 42, 2506 (1909).

[9] *Ann.*, 94, 225 (1855).

A 10-inch iron pipe, 12 inches long and threaded at both ends, was fitted with two cast-iron caps. To the upper cap there was attached a thermometer well, safety valve, and outlet tube consisting of an iron pipe about 3 inches long into which was inserted a glass tube 10 inches long, the joint being carefully sealed. An inverted U-shaped tube served to connect the apparatus with a block-tin coil condenser. Connections 1 and 2 were short pieces of thick-walled rubber tubing. In case the reaction mixture began to foam the U-tube could be raised easily and thus prevent the reaction mixture from flowing into the coil.

A Fletcher burner was placed under the apparatus and four Méker burners, clamped in horizontal positions, were used to apply heat near the top of the apparatus.

A number of experiments were carried out, in some instances with 2$^3/_4$ pounds of ammonium mucate, intimately mixed with an equal weight of hot glycerol, in other cases with 5$^1/_2$ pounds of the ammonium salt and 5$^1/_2$ pounds of glycerol. Pyrrole began to distil after the apparatus had been heated for about 40 minutes and 3 to 4 hours were usually required to complete the process. The crude pyrrole was purified as described above. The yields of pure pyrrole which were obtained in the last eight experiments were as follows: from 2$^3/_4$ pounds of ammonium mucate 41, 42, 42, and 45 per cent; from 5$^1/_2$ pounds of ammonium salt 45, 41, 44, and 51 per cent, respectively.

There seems to be no reason why the preparation of pyrrole by the above method could not be carried out just as successfully on a much larger scale.

Identification of Pyrrole

The pyrrole prepared in the manner described above boiled at 127–130° C. under 745 mm. pressure. In order to make certain of the identity of this material, a small portion was boiled with triphenylcarbinol in the presence of acetic acid. According to Khotinsky,[10] triphenylmethyl pyrrole (m. p. 253° C.) is formed quantitatively after a short time. The writers obtained a compound which, when heated, began to darken about 230° C. and melted with decomposition at 252° C. A specimen of pyrrole was separated from bone oil.[11] This material, when allowed to react with triphenylcarbinol, yielded a compound identical with that described above (mixed m. p. 252–253° C.).

Function of Glycerol

The function of the glycerol in this process seems to be at least twofold. Since ammonia is quite soluble in cold glycerol, the hot glycerol in the reaction mixture undoubtedly acts to some extent as the solvent for ammonia, as Khotinsky has suggested, and thus the ammonia necessary for the reaction remains in the apparatus longer than would be the case if no solvent were present. Furthermore, the glycerol prevents caking of the reaction mixture and permits the heat to be distributed more evenly throughout the reacting mass.

[10] *Ber.*, **42**, 3104 (1909).

[11] Ciamician and Dennstedt, *Ber.*, **19**, 173 (1886).

A Study of Auto-Ignition Temperatures[1]

By Henry James Masson and William F. Hamilton[2]

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A study has been made of the various factors affecting auto-ignition temperatures and as a result a new form of apparatus has been developed of high accuracy and sensitivity together with simplicity of construction and operation. The auto-ignition temperatures of a number of pure substances in air at normal pressure have been determined and their significance indicated. The apparatus and technic may be modified to determine the auto-ignition temperatures of solids and gases in any surrounding atmosphere at ordinary or increased pressures.

THE increasing use of liquid fuels for both internal and external combustion has directed attention to a more intimate study of their combustion as influenced by chemical and physical characteristics. Among the many investigations which have been made, those concerning the determination of the so-called spontaneous or auto-ignition temperature seem to possess those prerequisites necessary to shed additional light upon the mechanism of combustion and the internal structure of fuels.

When a series of drops of a combustible liquid is allowed to fall upon a surface, the temperature of which is progressively changed after each drop, a minimum temperature is ultimately reached at which the drop will burst into flame immediately after it makes contact with the surface. This temperature has been termed the "Zündpunkt" and later the "spontaneous" or "auto-ignition" temperature. The temperature so determined is relative and depends upon a number of variables, it being necessary to state the nature of each in any series of determinations. In what is to follow the shorter term "ignition" will be used instead of the longer terms given above.

Previous Work

The literature contains references to early studies in the field of ignition temperatures, but the data are frequently of such a character as to make appraisal difficult and in some cases impossible. For the proper interpretation of ignition data all the conditions surrounding the determination must be given. The earliest available determinations of ignition temperatures were made by Holm[1,*] in 1913. By allowing drops to fall upon a heated porcelain surface, the temperature of which was measured by means of a thermocouple, the ignition temperatures, in air, at normal pressure, of a number of the common liquid fuels were determined. Holm found, in general, that simplicity of molecular structure is associated with high ignition temperature, also that the ignition temperature is dependent upon the heat of decomposition and the activity of free valences at the moment of splitting apart or rearrangement. He also suggests that the ease with which substances undergo molecular change influences the ignition temperature.

The value of such determinations as a means of testing the usefulness of fuels for the Diesel engine was pointed out by Constam and Schläpfer,[2] who allowed drops of various fuels to fall into a platinum crucible imbedded in a sand bath which was heated by means of a gas flame, the temperatures being measured by means of a thermocouple. As great accuracy was not attained and the composition of the fuels not given, the results are difficult to evaluate.

H. Moore[3,4] while engaged in the study of fuels for use in the Diesel engine, developed an improved form of apparatus for measuring ignition temperatures. His apparatus consisted essentially of a platinum crucible imbedded in a steel block which

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[1] Presented under the title "A Study of the Spontaneous Ignition Temperatures of Various Liquids" before the Division of Gas and Fuel Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Submitted by Mr. Hamilton in partial fulfilment of the requirement for the degree of master of science in chemical engineering.

* Numbers refer to the bibliography at the end of article.

was heated from below by means of a gas flame. Temperatures were measured by means of a thermocouple inserted in a well drilled close to the crucible. Dry, preheated air or oxygen was delivered at constant velocity to the crucible by means of a coiled tube inserted in a well drilled in the steel block at the same level as the crucible, thereby delivering air or oxygen at the same temperature as the crucible. The apparatus designed by Moore has since become standard and has been used, with slight modification, by practically all subsequent observers. From his observations Moore concluded that (*a*) simple molecules have higher ignition temperatures than similar compounds containing more complex molecules, (*b*) aromatic compounds have higher ignition temperatures than aliphatic compounds, (*c*) unsaturated hydrocarbons have lower ignition temperatures than corresponding saturated hydrocarbons, and (*d*) ignition temperatures in air are higher than those in oxygen.

Tausz and Schulte[5,6] have extended the conditions surrounding the determination of ignition temperatures and obtained valuable data on many pure substances and commercial fuels, both in air and in oxygen under normal and increased pressures. Their apparatus was a modification of that of Moore, but the results vary somewhat from those obtained by Moore. Of interest is the effect of increased pressure, which is to lower the ignition temperature. This is in accordance with general theory, as the frequency of collision of the various molecules concerned is increased. The effect of increased pressure is of importance in internal-combustion engines, in which the explosive mixture is compressed before ignition by a spark takes place. The effect of compression is to increase the temperature of the explosive mixture. If preignition is to be avoided it is necessary to choose a fuel which will withstand this compression. The ignition temperature will set an upper limit of allowable compression before ignition by means of the spark.

Sinnott and B. Moore,[7] using a modification of the Moore apparatus and technic, studied the ignition temperatures of various coals and ascertained approximately their liability of spontaneous combustion.

The measurement of ignition temperature has been proposed as a new test for gasolines, but as yet the test has not been used commercially because further research must be carried on before they become entirely practical.[8,9,10] Additional investigations in the field of ignition temperatures have been carried on by Wollers and Emke,[11] Ormandy,[12] Alt,[13] Weerman,[14] Egerton and Gates,[15] and Daiber.[16]

It has been suggested by various observers[9,11,14,15,17 to 24] that ignition temperatures are related to the detonation characteristics of fuel in the internal-combustion engine, but just what the relationship is remains still a matter of conjecture. In a subsequent paper, in which the results of a study of the ignition temperatures of gasolines of known "knock" rating will be reported, a theory relating ignition temperatures and detonation will be developed.

Experimental

The ignition temperature has been defined [25,26] as the lowest temperature at which heat is generated by combustion faster than heat is lost to the surroundings and combustion thus becomes autogenous or self-propellent. In the case of liquid fuels the following experimental definition was used as the basis for the determinations which follow: "The ignition temperature is the lowest temperature at which a drop of definite size will burst into flame when brought in contact with a heated surface under definite circumstances."

Determinations of ignition temperatures in an apparatus similar to that of Moore[4] and others demonstrated the impossibility of obtaining concordant results because of inherent errors in the apparatus and manipulation. The study of ignition temperatures in the liquid phase involves a consideration of the following:

(1) Composition of substance dropped on surface
(2) Measurement of surface temperature
(3) Sensitivity of surface temperature
(4) Composition, physical character, and construction of surface
(5) Method of heating
(6) Temperature of gas surrounding surface
(7) Composition of gas surrounding surface
(8) Pressure of gas surrounding surface
(9) Size of drop
(10) Velocity of drop at time of contact
(11) Time interval between contact and flash
(12) Direction of approach to ignition temperature

The wide variations shown in the results of different observers, when working with the same substance, may be traced to a neglect of one or more of these factors. In this investigation every effort was made to keep all these factors constant except composition, which was the independent variable, and ignition temperature, which was the dependent variable. Some of the other factors involved were examined in a preliminary way but not completely; they will be the subject of future investigations. As the ignition temperature is in many cases very sensitive to the presence of small amounts of foreign substances, only pure materials were studied.

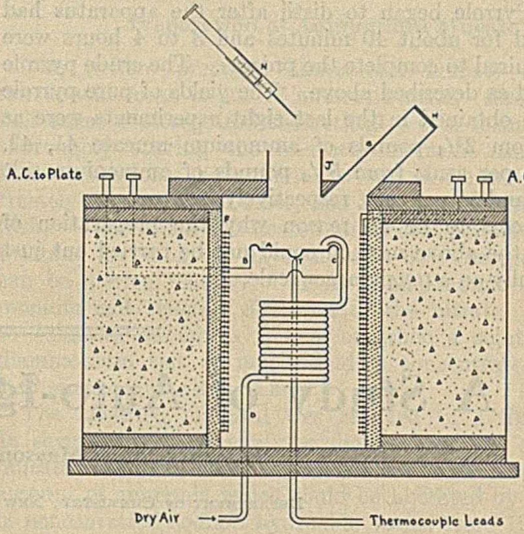

Figure 1—Apparatus for Determining the Auto-Ignition Temperatures of Liquid Fuels

Apparatus—After many modifications the form of apparatus shown in Figure 1 was evolved. In developing this form attention was concentrated on the accurate measurement of the surface temperature. By allowing the drop to fall essentially on the hot junction of a thermocouple, an accurate and sensitive measurement was obtained. As the heating element a cylindrical electric resistance furnace, *F*, 4 inches (10 cm.) in diameter and 6 inches (15 cm.) long, was constructed. When completed the over-all dimensions were approximately 6 by 8 inches (15 by 20 cm.). The surface selected consisted of a circular platinum plate, *A*, 1.5 inches in diameter and weighing 9 grams. An indentation was formed at the center to which was welded the hot junction of a Pt–Pt10%Rh thermocouple, *T*. The cold junction was set in a thermos bottle filled with ice to maintain a temperature of 0° C. Temperatures were read on a very sensitive millivoltmeter especially built to indicate temperatures between 650° and 1400° F. (343° and 760° C.). The thermocouple was calibrated by the manufacturer. Heavy platinum wires, *B* and *C*, covered with Impervite insulators were welded to the edges of the plate and alternating current was used as a means of superheating the plate. A length of nickel tubing, *D*, entered from the base of the furnace and coiled around, ending just above the edge of the plate. It was used to deliver air to the surface and remove the products of combustion. The air passed into the furnace was dried by means of sulfuric acid.

A demountable alundum cover was placed on the top of the furnace. This supported a quartz "look tube," *G*, which was provided with a magnifying glass, *H*, focused on the platinum plate. In the center of the alundum cover another piece of quartz tubing, *J*, was placed. This served as an opening for the introduction of the drops.

Drops of constant size were obtained by gravity flow from an ordinary hypodermic needle, *N*, The barrel of the needle served as a reservoir for the liquid, while drops of various sizes were obtained by the use of different-sized needles. Each needle was calibrated by weighing a given number of drops delivered as in the actual determinations. In practice the individual drops were found to show little variation in size and ignition temperatures were found to be duplicable to within 1° F. (0.55° C.) for any given liquid and needle. The height of fall of the drop was kept constant in all cases at 4 inches (10 cm.).

PROCEDURE FOR MAKING MEASUREMENTS—The furnace temperature is slowly raised and regulated by means of the rheostats. As the temperature approaches the ignition region as indicated by preliminary tests, a single drop of liquid is allowed to fall into the depression of the plate. The number of degrees drop in temperature due to the cooling effect and the number of degrees rise due to surface combustion are noted. This process is continued at regular intervals of temperature rise until a flash is seen within 1 second after the drop makes contact with the surface. After an approximate ignition point is ascertained the furnace temperature is lowered about 10° F. (5.5° C.) and held as nearly constant as possible at this value. The alternating current through the plate is then turned on and the temperature of the plate very slowly raised until ignition takes place. The plate is then raised 15° to 20° F. (8° to 11° C.) above this value and the temperature slowly lowered until ignition takes place. By repeating this procedure a number of times for a given substance the final ignition temperature is determined to the nearest degree. After each drop the stream of dry air is introduced to remove the products of oxidation. During the actual determination no movement of air over the plate from the tube is permitted. The readings thus obtained are constant and sharp; for example, at 1211° F. there was no flash with benzene, but at 1212° F. a flash resulted about 1 second after the drop made contact with the plate. The temperature of the plate just before the flash takes place is reported as the ignition temperature.

Typical Data Sheet

Substance: Benzene Specific gravity: 0.874
Needle No. 1
Weight of one drop: 0.00345 gram

TEMPERATURE OF PLATE	PYROMETER Drop	PYROMETER Rise	TIME OF FLASH	REMARKS
° *F.*	° *F.*	° *F.*	*Seconds*	
1185	5	20	.	No flash
1195	5	20	.	No flash
1200	5	19	.	No flash
1205	4	19	.	No flash
1210	3	10	.	No flash
1211	3	17	.	No flash
1212	2	10	1	Flash
1211	3	17	.	No flash
1212	2	9	1	Flash

RESULTS—The results of the determinations are given in Table I, in which the various substances studied have been arranged in the order of increasing ignition temperatures.

Discussion of Results

The auto-ignition temperatures determined as described must be thought of as relative and not absolute. The results differ considerably from those of other observers,[1,5,7] being in general higher although the same general sequence of increasing ignition temperatures is maintained. It is difficult to explain this difference other than as being due to the radically different types of apparatus used. Also the method of measuring the temperature used by other observers was indirect, whereas the method followed in this investigation was direct. In the present investigation attention was centered on the determination of the ignition temperatures of pure substances in the hope that some relationship to known physical or chemical properties might be found whereby the ignition temperature could be calculated. No regular or periodic relationship was found connecting ignition temperatures and molecular weight, specific gravity, boiling point, heat of combustion, heat of formation, vapor pressure, etc. However, the writers are of the opinion that there is a relationship between ignition temperatures and some property of combustible materials which is at present unknown or only partially so. It is assumed that when the drop hits the surface it is the film of vapor surrounding the drop which undergoes the combustion. It is assumed also that the oxidation is a progressive action passing from one oxidation product to another, the final products being carbon dioxide and water. That is, the mechanism of the combustion is best described by the "hydroxylation" theory.[27,28] It is suggested that those substances which combine readily with oxygen at high temperatures to form an unstable "oxygenated" or "hydroxylated" compound will have low ignition temperatures and the ignition temperature will rise in proportion to the difficulty of adding oxygen and decomposing the intermediate oxygenated compounds. The fact that the ignition temperature is lower in pure oxygen lends some support to this point of view. However, progressive oxidation of the original molecule is not the only possible or probable action taking place. The molecule may be "cracked" to give saturated and unsaturated hydrocarbons of lower molecular weight which then undergo progressive oxidation. There are, therefore, two possible courses for the reactions, resulting in a "race" between hydroxylation and thermal decomposition. It would seem, therefore, that a study of the foregoing factors might throw some light on the subject of ignition temperatures.

Table I

SUBSTANCE, IN AIR AT NORMAL PRESSURE	AUTO-IGNITION TEMPERATURE ° *F.*	° *C.*
Carbon bisulfide	Below 650[a]	343
n-Heptane	844	451
n-Octane	856	458
Monoethylaniline	895	479
Ether, ethyl	908	487
Alcohol, benzyl	935	501
Formic acid	940	504
Alcohol, amyl	965	519
n-Hexane	968	520
o-Toluidine	999	537
Alcohol, propyl	1004	540
Alcohol, isobutyl	1007	542
Ethyl benzene	1027	553
Nitrobenzene	1033	556
2,2,4-Trimethylpentane	1041	560
Alcohol, ethyl	1054	568
Alcohol, methyl	1065	574
Pentane	1074	579
m-Toluidine	1075	580
Benzyl acetate	1091	588
o-Cresol	1110	599
Acetic acid	1110	599
p-Xylene	1145	618
Alcohol, isopropyl	1148	620
Aniline	1148	620
m-Cresol	1158	626
Toluene	1172	633
Benzene	1212	656

[a] Lowest reading of pyrometer.

Experimental work is now in progress involving the study of the auto-ignition temperature of solids, liquids, and gases under different pressures and composition of the surrounding gas. A study is being made also of the relationship between auto-ignition temperatures and the "knock" characteristics of various liquid fuels of known "knock" rating. This study includes the effect of "knock" inducers and suppressors.

Acknowledgment

The authors wish to express their thanks to the Chas. Engelhard Company, and especially to Mr. Hebbler, for the skilful construction of the plate and thermocouple, its painstaking calibration, and for the kind coöperation and interest taken in the work at all times.

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Germicidal Efficiency of Sodium Hydroxide, Sodium Carbonate, and Trisodium Phosphate at the Same H-Ion Concentration[1,2]

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NUMEROUS alkali washing compounds are on the market for use in mechanical washing machines in the carbonated beverage and dairy industries. The role of these compounds is twofold—as detergents for cleansing the bottles of visible dirt; and as germicides to destroy objectionable microörganisms. The regulations of the health and food departments are aimed primarily at the bacterial phase of bottle-washing, on the assumption that conditions which will render a bottle free from objectionable bacteria (for practical purposes sterile) will also yield a satisfactory container from the standpoint of cleanliness. The minimum concentration of alkali, as determined by titration with a standard acid, is specified in these regulations, but there is no evidence that the titratable alkalinity of two alkalies is even an approximate measure of their relative germicidal powers. Thus, in some experiments which will be reported in detail in another paper it was observed that at 70° C. it required 37 minutes to kill one million bacterial spores with 0.55 per cent sodium hydroxide, whereas 1 per cent trisodium phosphate (equivalent to about 0.66 per cent sodium hydroxide by methyl orange) required 210 minutes, and 5.3 per cent sodium carbonate (equivalent to approximately 4.0 per cent sodium hydroxide by methyl orange) took 120 minutes to effect practical sterility. Evidently the titratable alkalinity is not an adequate measure of the relative germicidal efficiency of different alkalies. It has been suggested that the H-ion concentration might be a more dependable index.

The following experiments were designed to ascertain the relative germicidal efficiencies of different alkalies at the same H-ion concentration (as determined electrometrically at 30° C.).

Technic

A suspension of dried bacterial spores[3] was employed in all of the experiments described. About 0.02- to 0.05-gram portions of the bacterial mixture were suspended in 10 cc. of sterile tap water and filtered through paper to remove clumps. This constituted the bacterial suspension employed for disinfection.

The test alkali (100 cc.) was placed in a 200-cc. round-bottom, three-neck Woulfe bottle, which was provided with a glass stirrer through the middle neck, the other openings being plugged with cotton. The entire apparatus was sterilized in the autoclave at 120° C. for 15 to 20 minutes. After the flask containing the alkali was cooled, it was placed in a de Khotinsky water bath and the stirrer set in motion, care being taken that no bubbles or foaming developed.

When the alkali attained and remained at the desired temperature, 1.0 cc. of the bacterial suspension was introduced under the surface of the liquid by means of a capillary pipet. At desired time intervals 5.0-cc. portions of the thoroughly stirred mixture were removed and inoculated into Erlenmeyer flasks containing 45.0 cc. of sulfuric acid (with methyl orange indicator) of a strength just sufficient to neutralize the alkali added. The effect of alkali and temperature was thus simultaneously stopped. The number of surviving bacteria was then determined by plating on nutrient agar.

All bacterial counts were calculated on the basis of 5.0 cc. of disinfecting mixture. It was aimed to employ a suspension giving an initial count of about one million per unit volume (5.0 cc.). The relative germicidal powers of the different alkalies were ascertained by determining the time required to kill 99.9 per cent of the exposed bacteria at a given temperature and hydrogen-ion concentration.

Experimental Results

A solution of sodium carbonate equivalent to a normal alkali gave an H-ion concentration of pH 11.35 at 30° C. A sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) of the same H-ion concentration was found to be equal to 0.0545 N alkali, and a sodium hydroxide solution of pH 11.34 was found to be 0.0065 N alkali. All titrations were with methyl orange, and the H-ion concentrations were determined electrometrically at

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[1] Received June 6, 1927.

[2] This study was made possible through a fellowship maintained by the American Bottlers of Carbonated Beverages at the Iowa State College, Ames, Ia.

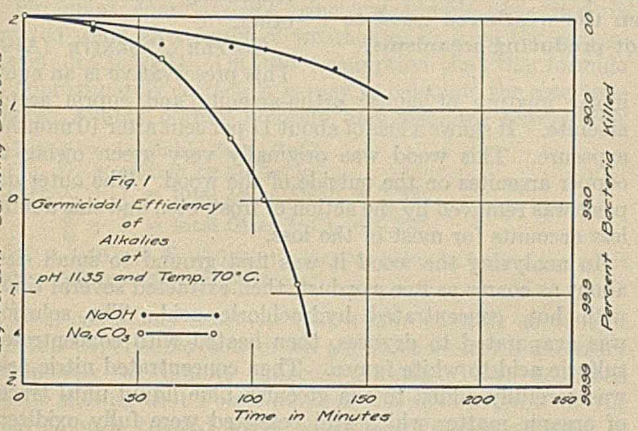
[3] *Iowa State College J. Science*, **1**, No. 4, pp. 379-394 (1927).

30° C. The germicidal effects of these alkalies were determined at 69–70° C.

Table I—Surviving Bacteria in Sodium Hydroxide and Sodium Carbonate of pH 11.35

Time	Surviving Bacteria in 5.0 cc.		Per Cent Surviving Bacteria		Log Per Cent Survivors	
	Na_2CO_3	NaOH	Na_2CO_3	NaOH	Na_2CO_3	NaOH
Minutes						
			TEMPERATURE, 69° C.			
0	900,000	900,000	100.0	100.0	2.000	2.000
30	543,000	748,000	60.3	83.0	1.780	1.919
60	214,000	662,000	23.8	73.5	1.377	1.866
75	91,500	630,000	10.2	70.0	1.009	1.845
90	38,500	504,000	4.28	56.0	0.632	1.748
100	27,800	420,000	3.09	46.7	0.490	1.669
110	15,800	324,000	1.76	36.0	0.246	1.556
130	6,800	192,000	0.76	21.3	$\bar{1}.881$	1.328
140	3,400	167,000	0.38	18.6	$\bar{1}.580$	1.270
			TEMPERATURE, 70° C.			
0	928,000	928,000	100.0	100.0	2.000	2.000
30	760,000	640,000	81.9	69.0	1.913	1.839
60	288,000	450,000	35.0	48.5	1.544	1.686
90	44,000	440,000	4.73	47.5	0.675	1.677
105	10,000	425,000	1.08	45.7	0.033	1.660
120	1,200	330,000	0.13	35.6	$\bar{1}.1106$	1.551
135	200	260,000	...	28.0	...	1.447

The results for sodium carbonate compared with sodium hydroxide are detailed in Table I for the carbonate and phosphate in Table II and shown graphically in Figures 1 and 2.



It is quite evident from Tables I and II that at pH 11.35 sodium carbonate was much more efficient than the phosphate and the phosphate was superior to the hydroxide. Thus, the killing times for the carbonate, phosphate, and hydroxide of sodium at a pH of 11.35 and temperature of 70° C. were 120, 163, and over 220 minutes, respectively.

Table II—Surviving Bacteria in Sodium Carbonate and Trisodium Phosphate of pH 11.35 at 70° C.

Time	Surviving Bacteria in 5.0 cc.		Per Cent Surviving Bacteria		Log Per Cent Surviving Bacteria	
	Na_2CO_3	Na_3PO_4	Na_2CO_3	Na_3PO_4	Na_2CO_3	Na_3PO_4
Minutes						
0	448,000	448,000	100.0	100.0	2.000	2.000
30	263,000	...	58.6	...	1.768	...
60	42,000	249,000	9.4	55.6	0.974	1.745
75	21,000	217,000	4.7	48.4	0.672	1.685
105	1,500	84,500	0.33	18.8	$\bar{1}.519$	1.275
120	225	33,500	...	7.5	...	0.875
135	...	13,700	...	3.0	...	0.477

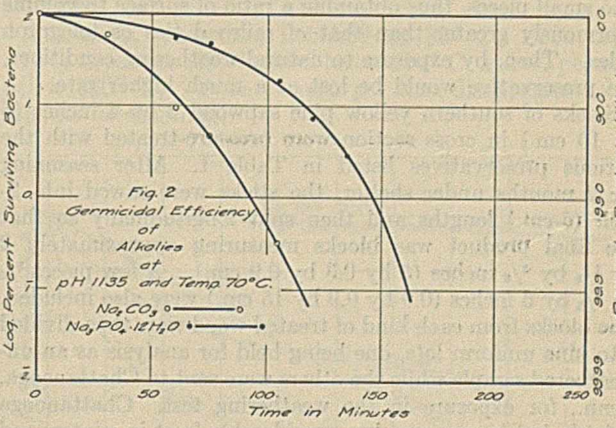
In another series of observations sodium hydroxide and phosphate were compared. A 0.5 *M* trisodium phosphate was taken as a basis for comparison, and its H-ion concentration at 30° C. was found to be pH 12.15. A preliminary test showed that this phosphate concentration killed a million spores in less than 10 minutes. A sodium hydroxide solution of pH 12.18, which titrated 0.1215 *N* alkali, was compared with the 0.5 *M* phosphate (1.065 *N* alkali as NaOH by titration) as to germicidal efficiency at 70° C. The results are shown in Table III and Figure 3.

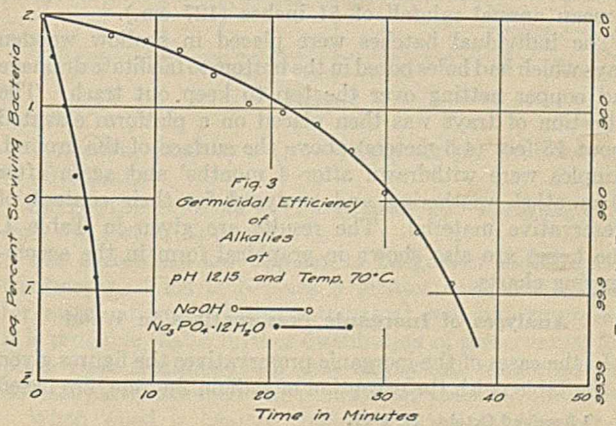
At pH 12.15 and 70° C. the trisodium phosphate was much more efficient than sodium hydroxide. Whereas the former effected a reduction of 99.9 per cent of the exposed bacteria in about 5 minutes, it required 36 minutes to effect the same reduction with the sodium hydroxide.

Table III—Surviving Bacteria in Sodium Hydroxide and Trisodium Phosphate of pH 12.15 to 12.18 at 70° C.

Time	Surviving Bacteria in 5.0 cc.		Per Cent Surviving Bacteria		Log Per Cent Surviving Bacteria	
	NaOH	Na_3PO_4	NaOH	Na_3PO_4	NaOH	Na_3PO_4
Minutes						
0	1,100,000	1,100,000	100.0	100.0	2.000	2.000
1	...	378,000	...	33.9	...	1.530
2	...	115,000	...	10.3	...	1.013
3	...	23,000	...	1.7	...	0.230
4	...	5,400	...	0.49	...	1.690
5	...	1,500	...	0.14	...	1.146
6	663,000	125	59.9	0.011	1.777	...
7	...	0	...		...	
9	570,000	0	51.5		1.712	
12	463,000	0	41.7		1.620	
15	248,000	0	22.3		1.348	
18	120,000		10.8		1.033	
21	87,800		8.9		0.949	
24	76,500		6.9		0.839	
27	40,500		3.62		0.559	
30	13,600		1.23		0.090	
33	.5,050		0.45		$\bar{1}.653$	
36	1,480		0.13		$\bar{1}.114$	
39	550		0.05		...	
42			...		...	

For a given alkali the killing time decreases with increasing pH, as may be readily observed by comparing trisodium phosphate, or hydroxide, at pH 11.35 and 12.15. Thus it will be noticed that at pH 12.15 sodium hydroxide practically effected sterilization (99.9 per cent killing) in 36 minutes, while at pH 11.35 numerous organisms were still alive after 200 minutes, and with the phosphate a killing time of 5 minutes at pH 12.15 was increased to 163 minutes at pH 11.35. The H-ion concentration, however, is not a dependable index of the relative germicidal efficiencies of different alkalies, as sodium phosphate, carbonate, and hydroxide at the same pH value showed variations of over 500 per cent in the killing time. It appears that factors other than the concentration





of hydroxyl (OH) ions are important in the germicidal effects of alkalies.

Conclusions

1—The germicidal efficiency of alkalies is influenced to a marked degree by factors other than the hydrogen-ion concentration.

2—For each of the alkalies studied, considered individually, the germicidal efficiency was a direct function of the hydrogen-ion concentration.

3—The hydrogen-ion concentration alone should not be considered as a dependable index of the germicidal efficiencies of different alkalies.

Experiments in Wood Preservation[1]

V—Weathering Tests on Treated Wood

By Leo Patrick Curtin, Bernard L. Kline, and William Thordarson

Engineering Laboratories, Western Union Telegraph Co., New York, N. Y.

Weathering tests are described in which wood treated with various preservatives was cut into small pieces and exposed in overhead trays to the action of wind, sun, and rain. Chemical analyses were made on wood so weathered to determine the loss of preservative caused by leaching, evaporation, and oxidation. Toxicity tests were also made on the weathered wood to determine its resistance to rot-producing organisms.

THE rate at which preservative material is lost from treated wood is a question of fundamental importance in wood preservation. If the preservative is a water-soluble salt, loss will occur by leaching if exposed to rains; if it is a volatile oil, vaporization will take place. In either case the resistance of the treated wood will progressively diminish and finally a condition will be reached which permits the wood-rotting organisms to gain a foothold. Since it seemed desirable to obtain data on this problem, accelerated tests were devised which duplicated field tests in every respect except in the rate at which preservative was lost from the treated wood.

The best method that suggested itself was to cut the wood into small pieces, thus obtaining a ratio of surface to volume enormously greater than that of railroad ties or telegraph poles. Then, by exposure to natural weathering conditions, the preservative would be lost at a much higher rate.

Sticks of southern yellow pine sapwood 2 by 4 inches (5 by 10 cm.) in cross section were pressure-treated with the various preservatives listed in Table I. After seasoning for 2 months under shelter, the sticks were sawed into 2-inch (5-cm.) lengths and then split longitudinally so that the final product was blocks measuring approximately 2 by $^1/_8$ by $^3/_8$ inches (5 by 0.3 by 0.9 cm.). A few pieces $^3/_8$ by $^3/_8$ by 6 inches (0.9 by 0.9 by 15 cm.) were also included. The blocks from each kind of treated wood were then divided into nine uniform lots, one being held for analysis as an unweathered sample while the others were sent to Chattanooga, Tenn., for exposure in the weathering test. Chattanooga is fairly hot in summer, has considerable frost in winter, and a mean annual rainfall of 51 inches (127 cm.).

The individual batches were placed in shallow wooden trays which had holes bored in the bottom to facilitate drainage and copper netting over the top to keep out trash. The collection of trays was then placed on a platform elevated about 15 feet (4.5 meters) above the surface of the ground. Samples were withdrawn after 4 months' and again after 10 months' weathering and analyzed for their content of preservative material. The results are given in Table I. The losses are also shown in graphical form in the accompanying charts.

Analyses of Inorganic Preservatives in Wood

In the cases of the inorganic preservatives the figures given in the table, with the exception of sodium fluoride, are based on the analyses of the metal ion. The values given in each case are the mean of three to six independent analyses, most of which checked reasonably well with each other.

Copper Arsenite (A)—This preservative is an equimolar mixture of cupric ortho-arsenite and cupric aceto-arsenite. It shows a loss of about 11 per cent after 10 months' exposure. This wood was originally very green owing to copper arsenites on the outside of the wood. The outer deposit was removed by the action of frost, etc., and this doubtless accounts for most of the loss.

In analyzing the wood it was first ground to small size, about as coarse as fine sawdust, then extracted several times with hot, concentrated hydrochloric acid. The solution was evaporated to dryness, then heated with concentrated sulfuric acid to white fumes. Then concentrated nitric acid was carefully added to the greenish blue liquid until traces of organic matter which still persisted were fully oxidized, the solution now being blue in color. A trace of ferric ion was removed by precipitation with ammonium hydroxide, the excess ammonia neutralized with acetic acid, and the cupric ion titrated by the standard potassium iodide–sodium thiosulfate method, using starch as an indicator.

In the preparation of the solution for the copper analysis the arsenic present was driven off as $AsCl_3$ and lost. In the determination of arsenic a 10-gram sample of treated wood was distilled with 250 cc. of concentrated hydrochloric acid. The distillate was condensed, diluted, and the trivalent arsenic oxidized to the pentavalent form with a large excess of hydrogen peroxide. The solution was then made ammoniacal and boiled for a few minutes. Magnesia mixture was added, which precipitated the arsenic as $MgNH_4AsO_4$. After standing overnight, the precipitate was filtered out in a Gooch crucible, ignited, and weighed as $Mg_2As_2O_7$. Two treatments with hydrogen peroxide are frequently necessary, as all traces of organic matter must be destroyed. Two analyses by this method showed the arsenic to be present in chemically equivalent quantities with respect to the copper. The analyses for arsenic in treatments *A*, *E*, and *F* were made only on the samples which had been weathered for 10 months.

Sodium Fluoride (*B*)—The ground wood was extracted with hot water and the fluoride in the filtrate determined as calcium fluoride. Wood treated with this preservative lost more than 95 per cent of the original treatment in 10 months' weathering.

Barium Carbonate (*C*)—The ground wood was extracted

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[1] Received October 17, 1927.

with dilute hydrochloric acid and the barium precipitated from the filtrate as sulfate. Ten months' weathering resulted in a loss of 54 per cent. This was much heavier than was anticipated, although it was expected that acids occurring naturally in the wood would cause some loss.

Zinc Chloride (*D*)—The zinc was extracted from the ground wood by digesting with dilute hydrochloric acid. The solution was evaporated to dryness and organic matter destroyed by heating with concentrated sulfuric and nitric acids. The solution was cooled and diluted, the remainder of the analysis being the standard potassium ferrocyanide uranium nitrate method. This was a very satisfactory analysis in this case and also with treatment *E*. About 91 per cent of the original zinc chloride had been washed from the wood at the end of 10 months.

Two analyses were made on the zinc chloride–treated wood which had been exposed for 10 months to determine its chloride content. This was of interest as indicative of the extent to which the zinc chloride had been hydrolyzed. Dilute sulfuric acid was used in the several successive extractions of the ground wood. The values were 0.890 and 0.883, the mean being 0.887 ounce per cubic foot or kilogram per cubic meter.

Bateman[2] considers the zinc oxychloride deposited in treated wood as a result of weathering to have the composition $ZnCl_2.5ZnO$. On the assumption that this formula is approximately correct, it is easy to calculate the zinc present as soluble normal chloride and insoluble oxychloride.

$$\begin{aligned} \text{Let } X &= \text{insoluble Zn as } ZnCl_2 \\ Y &= \text{soluble Zn as } ZnCl_2 \\ \text{Then } X + Y &= \text{total Zn as } ZnCl_2 = 2.22 \\ \frac{X}{6} + Y &= \text{total Cl as } ZnCl_2 = 0.887 \end{aligned}$$

$X = 1.60$ and $Y = 0.62$, the figures being in ounces per cubic foot or kilograms per cubic meter.

It is commonly assumed that a zinc chloride content of 4.8 ounces per cubic foot (or kg. per cubic meter) is necessary completely to inhibit fungous growth. Tests described below showed that *Fomes annosus* was able to grow on the zinc chloride–treated wood which had been weathered 10 months. There was strong partial inhibition, however, much greater than could be accounted for by the insignificant quantity of zinc chloride present and about what would be expected if it is assumed that the oxychloride is equal to the chloride as a fungicide.

Zinc Meta-Arsenite (*E*)—The zinc was extracted from the wood with hot concentrated hydrochloric acid, which also vaporized the arsenic as arsenious chloride. The remainder of the analysis is described in connection with treatment *D*. The zinc analysis in treatments *D* and *E* was checked by a gravimetric method in which mercuric thiocyanate is used to precipitate the zinc. Satisfactory checks were obtained in both cases. Three analyses of the arsenic content of treatment *E* showed that arsenic chemically equivalent to the zinc content was present and that no measurable loss of zinc meta-arsenite occurred in 10 months' exposure.

Copper Aceto-Arsenite (*F*)—The analyses in this case were identical with those made in connection with treatment *A*. After 10 months' weathering 9 per cent of the preservative had been lost from the wood.

Analyses of Organic Preservatives in Wood

All organic preservatives were extracted from the ground wood using benzene at the boiling temperature as a solvent. An extraction thimble was used and the washing continued for 30 minutes after the benzene commenced to run clear. The petroleum-treated wood looked clean and bright after the extraction, while the creosote-treated wood appeared grayish, owing to the small quantity of benzene-insoluble matter which is normally present in creosote.

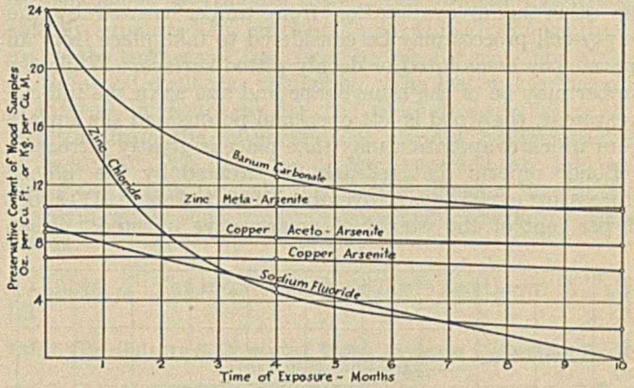

Figure 1

Untreated wood cut from the same pieces which were used for the creosote and petroleum treatments was ground and then extracted with benzene. The average of five extractions showed that resinous material equal to 3 per cent by weight was removed from the wood. A correction was therefore made on all oil extractions to compensate for this factor.

Petroleum, Density at 38° C., 0.936 (*HA*)—This was a high-boiling oil, practically none of it distilling below 270° C. Eight per cent was lost in the 10 months' weathering period.

Petroleum, Density at 38° C., 0.905 (*HS*)—Five per cent of this oil distilled over below 270° C. and 35 per cent below 355° C. Ten months' weathering resulted in a loss of 19 per cent.

Creosote, English, Density at 38° C., 1.068 (*I*)—Thirty-three per cent distilled below 270° C. and 85 per cent below 360° C. Forty-two per cent disappeared in 10 months' exposure.

Creosote, American, Density at 38° C., 1.056 (*J*)—Thirty-seven per cent distilled below 270° C. and 80 per cent below 360° C. Twenty-seven per cent disappeared in 10 months' weathering.

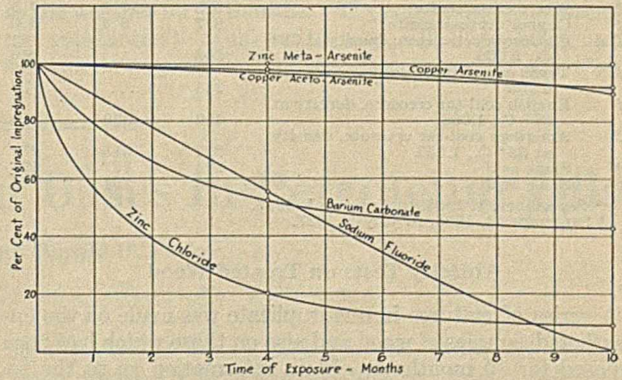

Figure 2

Creosote, Same as *J* (*N*)—Thirty-six per cent was lost in 10 months.

Creosote, Same as *J* (Treatment *O*)—Forty-eight per cent was lost in 10 months.

The percentage loss appears to be greater in the lighter treatments. This is because a greater surface is exposed for evaporation. While treatment *O* was not empty-cell, it is probable that a further distribution of preservative took place after treatment and that empty-cell conditions were at least partly attained when the system reached equilibrium.

When wood is heavily treated with oil by the full-cell

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[2] *Am. Ry. Eng. Assocn., Bull.* **227**.

method, it may be considered that evaporation is taking place from the surface of a cylinder, in the case of a pole, or from a body of plane surfaces, in the case of a sawn tie. On the other hand, evaporation from timber treated by the empty-cell process may be considered to take place from an enormously convoluted or deeply pitted surface. While the timber may be of the same shape and size as in the full-cell treatment, the wood is left open and porous and the surface from which evaporation may take place is greatly increased.

Bond[3] reports that red-oak ties treated by the full-cell process lost in 200 days (November, 1910, to June, 1911) about 19 per cent of the weight of preservative injected. When similar ties were treated by an empty-cell process the loss in the same period was about 52.7 per cent. Maple ties treated by the full-cell process lost in 105 days (March to June, 1911) 13.4 per cent of the weight of creosote injected. When similar ties were treated by an empty-cell process they lost in the same time 23 per cent. As these ties were all air-seasoned and at approximately the same moisture content, little of this loss can be attributed to evaporation of water.

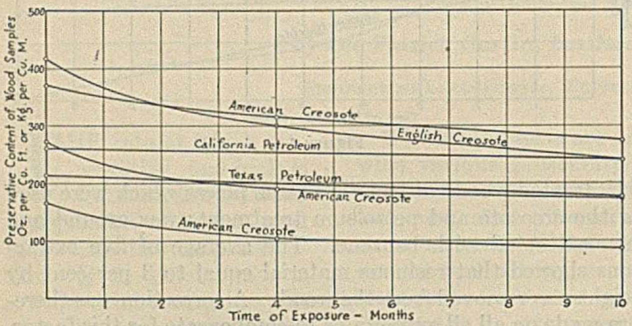

Figure 3

Table I—Quantity of Preservative in the Wood
(Ounces per cubic foot or kilograms per cubic meter)

TREATMENT	PRESERVATIVE	UNWEATHERED	AFTER EXPOSURE 4 Months[a]	AFTER EXPOSURE 10 Months[b]
A	Copper arsenite	7.0	6.9	6.2
B	Sodium fluoride	9.2	5.1	Trace
C	Barium carbonate	24.0	12.6	10.3
D	Zinc chloride	23.0	4.6	2.2
E	Zinc meta-arsenite	10.5	10.6	10.5
F	Copper aceto-arsenite	8.7	8.4	8.0
HA	California petroleum, density at 38° C., 0.936	260	...	240
HS	Texas petroleum, density at 38° C., 0.905	214	...	176
I	English coal-tar creosote, density at 38° C., 1.068	419	300	240
J	American coal-tar creosote, density at 38° C., 1.056	371	315	274
N	Same as *J*	274	187	174
O	Same as *J*	166	104	87

[a] September, 1, 1926, to January 1, 1927.
[b] September 1, 1926, to July 1, 1927.

Toxicity Tests on Treated Wood

A series of cultures in quadruplicate was made on the unweathered samples of wood and also on those which had been exposed for 10 months to obtain information as to the resistance of the exposed wood to fungous attack. Three types of cultures were used, which will be designated as *X*, *Y*, and *Z*.

Type *X* was made by introducing long sticks of wood into test tubes containing 5 cc. of nutrient gel in the bottom. Photographs of similar cultures are shown in the second paper of this series.[4] Type *Y* was made by arranging four smaller sticks in the form of a square in a Petri dish on the bottom of which were 10 cc. of nutrient gel. Type *Z* was a suspension of ground wood in standard agar–malt sirup gel. This last type was of no importance in the cases of the less toxic preservatives, since it was possible for the fungus to grow in the gel between particles of wood. In cases where complete inhibition was accomplished, however, the results were significant.

The oil-treated wood was not sterilized since the heating would remove considerable preservative from the wood. Otherwise the cultures were made under aseptic conditions, a transplant of the fungus *Fomes annosus* being placed in each culture.

The cultures containing unweathered wood, with the exception of the petroleum-treated material, all showed excellent resistance to fungous attack. This, of course, was expected.

The next series was made with wood which had been weathered for 10 months, and these will be discussed in detail.

COPPER ARSENITE (*A*)—Cultures *X* and *Y* showed the wood to be fully resistant to attack.

Culture *Z:* Four 20-gram cultures in Petri dishes were prepared which contained 1.67, 3.65, 6.03, and 8.00 grams treated wood. Disregarding the small loss of preservative due to weathering, these cultures contained 0.10, 0.20, 0.30, and 0.40 per cent of copper arsenite. After 4 weeks light growth had taken place on the 0.10 and 0.20 cultures, the transplant was alive but had made no progress on the 0.30 culture, while in the 0.40 culture two transplants had died.

SODIUM FLUORIDE (TREATMENT *B*)—Cultures *X* and *Y:* The wood was freely attacked by the fungus.

Culture *Z:* Two cultures were made containing 6 and 9 grams ground wood with enough agar nutrient to make the total weight 20 grams. The fungus grew well in both cultures, as was to be expected from the negligible amount of preservative left in the wood. It is difficult to make cultures containing more than 40 per cent ground wood as the culture tends to become granular and non-coherent.

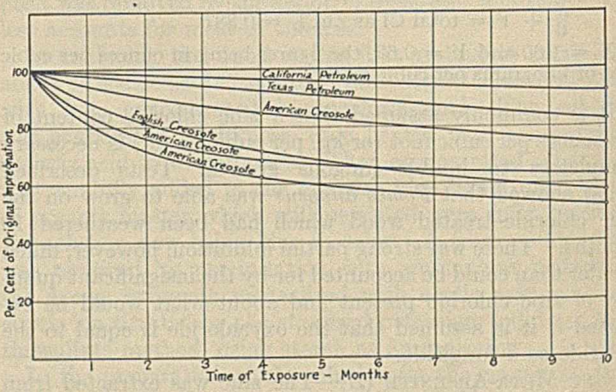

Figure 4

BARIUM CARBONATE (*C*)—Culture *X:* The fungus made a delicate growth on the sticks to a height of 3 cm. and then died. This growth was apparently caused by nutrient which had ascended the sticks by capillarity. There was no evidence that the wood had been attacked.

Culture *Y* gave substantially the same results.

Culture *Z:* These were made with 7 and 8 grams of wood in a total weight of 20 grams. The fungus grew fairly well in the 7-gram culture and poorly in the 8-gram culture.

ZINC CHLORIDE (*D*)—Culture *X:* Light attack to a height of 3 cm. on three sticks. On one stick growth continued for a distance of 12 cm. At the end of a month the fungus on the first three sticks was dying.

Culture *Y:* Very light attack.

Culture *Z:* Delicate but healthy growth completely filled the Petri dishes at end of five weeks. Cultures contained 6 and 7.8 grams of wood in total of 20 grams.

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[3] *U. S. Forest Service, Bull.* **123**.
[4] THIS JOURNAL, **19**, 993 (1927).

Zinc Meta-Arsenite (*E*)—Culture *X* showed in all cases perfect resistance to attack. The fungus grew well in the gel but, after reaching the wood, turned yellow and died.

Culture *Y* showed similar results.

Culture *Z:* Results for this culture are given in Table II.

Table II—Culture *Z*, Zinc Meta-Arsenite, 20-Gram Cultures

Weight of Wood in Culture	$Zn(AsO_2)_2$ in Culture	Condition after 6 Weeks
Grams	*Per cent*	
1.301	0.1	Light growth on surface of culture
2.784	0.2	Feeble growth
4.488	0.3	Feeble growth to 3 mm. from culture, then no further progress
6.570	0.4	Complete inhibition

Total inhibition was obtained in this type of culture with wood treated with arsenites of copper or zinc. This is a remarkable demonstration of the toxicity of the insoluble arsenites. Most of the preservative was inside the wood, therefore taking little or no part in the inhibition of the fungus. In spite of this, growth was prevented in the nutrient gel by ground wood containing only four or five times the killing dose as determined in cultures containing the pure preservative in powder form.

Copper Aceto-Arsenite (*F*)—Cultures *X* and *Y* showed perfect resistance to fungus attack.

Culture *Z* gave results identical with those obtained in the cases of treatments *A* and *E*. Growth was completely inhibited in a 20-gram culture containing 5.91 grams treated wood or slightly less than 0.3 per cent of preservative.

Toxicity Tests on Oil-Treated Wood

Cultures *X* and *Y* showed vigorous growth of the fungus on the petroleum-treated sticks, treatments *HA* and *HS*. There was no apparent difference between the weathered and unweathered wood.

Coal-Tar Creosote (*I*, *J*, *N*, and *O*)—Cultures *X* and *Y* on the unweathered material showed the wood to be of high toxicity. It was impossible to maintain a living transplant of the fungus in the presence of the treated wood; it was killed in 24 to 48 hours by the poisonous fumes emanating from the wood, even when separated by a distance of 1 cm. from physical contact with the wood.

Cultures *X* and *Y* on the wood which had weathered for 10 months showed a greatly reduced toxicity. In every case the fungus grew vigorously in the nutrient gel and in culture *X* ascended the sticks to a height of 3 to 4 cm. It at first appeared that the fungus was attacking the wood. After 2 weeks, however, the growth stopped, the fungus turned yellow and finally died. This growth was almost entirely supported by nutrient liquid which had been drawn up on the surfaces of the sticks by capillarity. The attack on the wood itself was negligible. The test was principally of interest in demonstrating the great decrease in toxicity resulting from the evaporation of the low boiling fraction of creosote. The behavior of the creosoted wood in this test gives reason for believing that weathering for another year will reduce the toxicity to a point which permits fungous attack.

Culture *Z:* The results for this culture are shown in Table III.

Table III—Culture *Z*, Creosoted Wood, 20-Gram Cultures, 4 Weeks' Test Total Inhibition

Treatment		Wood in Culture	Preservative in Culture	Remarks
		Grams	*Per cent*	
I	Unweathered	0.615	2.0	Clean culture; growth at 0.5 per cent
	Weathered	4.51	7.0	Growth at 4.0 per cent; heavy growth of mold
J	Unweathered	0.714	2.0	No growth; no mold
	Weathered	4.57	8.0	No growth; very slight growth at 4.0 per cent; some mold
N	Unweathered	0.235	0.5	No growth; no molds
	Weathered	5.82	6.0	This culture permitted a few mm. growth; growth also at 4 per cent; heavy growth of molds
O	Unweathered	1.67	2.0	Growth at 0.5 per cent; no mold
	Weathered	8.30	4.0	Growth at 3.0 per cent; vigorous growth of molds

Summary

A 10 months' weathering test on treated wood cut into small pieces shows the following:

Preservative	Loss	Preservative	Loss
	Per cent		*Per cent*
Zinc meta-arsenite	0.0	Barium carbonate	54.0
Copper aceto-arsenite	9.0	Zinc chloride	91.0
Copper arsenite	11.0	Sodium fluoride	95 to 99
Creosote	27 to 48	Petroleum	8 to 19

The preservatives are listed in the order of their toxicity as shown by tests on treated wood which has been exposed to the weather for 10 months. The copper and zinc arsenites are substantially equal in toxicity, all three being much superior in toxicity and permanence to any of the others.

Determination of Nitrogen Bases in Petroleum Oils[1]

By Ralph H. McKee and Harold H. Parker

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Sulfuric acid absorption has been extensively used as a rapid analytical method for determining the amount of unsaturated compounds in oils. Botkin,[2] among others, has commented upon its unreliability, particularly with shale oils, as the acid absorbs not only olefinic hydrocarbons but nitrogen bases as well. The nitrogen bases are present in shale petroleum materials as methylated pyridine and quinoline derivatives, up to 15 per cent. Franks[3] has advocated that the oil be reported as "per cent saturates," but this use of the term may easily lead to wrong interpretation of retorting, refining, or cracking experiments, for the nitrogen compounds are very different chemically from the unsaturates. The importance of a rapid test through which they may be studied separately is therefore evident.

Franks[4] determined the nitrogen bases in shale distillates by an absorption method using approximately 28 per cent hydrochloric acid; but he gives no data to show the accuracy of the method. Accordingly work was carried out with different prepared solutions to determine, first, whether or not concentrated sulfuric acid completely absorbed both unsaturates and nitrogen bases, and, second, whether hydrochloric acid reacted only with the nitrogen bases. Twenty-five per cent acetic acid was later tried. No attempt

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[1] Received July 12, 1927.

[2] *Chem. Met. Eng.*, **26**, 445, 398 (1922); **24**, 876 (1921).

[3] *Ibid.*, **24**, 561 (1921).

[4] *Chem. Met. Eng.*, **25**, 734 (1921).

was made to make the method exactly quantitative, as inaccuracies in reading, polymerization, and solution of oil in acid make these centrifugal absorption methods, at best, accurate only to about 2 per cent. Tests were run on the following solutions: (1) a mixture of hexane, amylene, and pyridine; (2) petroleum gasoline; (3) petroleum gasoline and pyridine; (4) petroleum gasoline and quinoline; (5) fraction below 275° C. from crude shale petroleum.

Methods

The method was essentially that recommended by Dean and Hill[5] for the sulfuric acid test for unsaturates. A standard Babcock test bottle with the neck having an approximate volume of 6 cc. graduated from 0 to 30 was used. Five centimeters of the oil were pipetted into the test bottle, cooled in ice water, and 10 cc., or 200 per cent by volume, of the acid carefully added. The bottle was then stoppered and, except with the acetic acid, allowed to remain in ice water for 30 minutes with occasional shaking. Where acetic acid was used, 10 cc. of glacial acid were added to the oil and the mixture shaken, diluted with water, and immediately centrifuged. Acid of the same strength (25 per cent) was next added to bring the reading within the range of the graduations and the tightly stoppered bottle placed in the centrifuge and whirled at about 1000 for 2 or 3 minutes. The percentage of nitrogen compounds was calculated from the amount absorbed as read from the graduated neck of the bottle. Each graduation represents 2 per cent by volume if we assume that the volume of the neck between 0 and 25 is 5 cc.

Results

The results are summarized in the accompanying table.

Analysis of Test Solutions for Unsaturates and Nitrogen Bases

Acid	Per Cent[a] Obs.	Per Cent[a] Calcd.
MIXTURE OF HEXANE, AMYLENE, AND PYRIDINE		
Concd. H_2SO_4	22	25
Concd. HCl	16	12
29% HCl	18	12
20% HCl	18	12
10% HCl[b]	22	12
WELL PETROLEUM GASOLINE		
Concd. H_2SO_4	12	..
Concd. H_2SO_4	10	..
Concd. H_2SO_4	12	..
Concd. H_2SO_4	12	..
Concd. H_2SO_4	12	..
Concd. H_2SO_4	13	..
25% acetic	0	0
25% acetic	0	0
25% acetic	0	0
25% acetic	0	0
Concd. HCl	2	0
Concd. HCl	0	0
26% HCl	0	0
26% HCl	1	0
4% HCl	0	0
4% HCl	2	0
20 PER CENT SOLUTION OF QUINOLINE IN WELL PETROLEUM GASOLINE		
Concd. H_2SO_4	30	30
Concd. H_2SO_4	30	30
25% acetic	20	20
25% acetic	21	20
16 PER CENT SOLUTION OF QUINOLINE IN WELL PETROLEUM GASOLINE		
Concd. H_2SO_4	24	26
Concd. H_2SO_4	25	26
Concd. H_2SO_4	24	26
Concd. H_2SO_4	24	26
25% acetic	16	16
25% acetic	20	16
25% acetic	16	16
25% acetic	16	16
GASOLINE SOLUTION CONTAINING QUINOLINE AFTER WASHING WITH H_2SO_4		
25% acetic	0	0
25% acetic	0	0
20 PER CENT SOLUTION OF QUINOLINE IN WELL PETROLEUM GASOLINE		
25% acetic	20	20
25% acetic	21	21
Concd. H_2SO_4	30	30
Concd. H_2SO_4	30	30
Concd. HCl	20	20
Concd. HCl	20	20
4% HCl	20	20
4% HCl	20	20
"TOPS" TO 275° C. FROM CRUDE SHALE PETROLEUM		
Concd. HCl	11	..
Concd. HCl	10	..
25% acetic	14	..
25% acetic	13	..

[a] The per cent corresponding to sulfuric acid treatment represents both unsaturates and nitrogen compounds, while the calculated values after hydrochloric and acetic acids include nitrogen compounds only.

[b] In this run the oil and acid mixture was allowed to stand overnight.

The first experiments were run with the test solution prepared in the laboratory from hexane, amylene, and pyridine. Such a mixture does not exactly duplicate conditions in well petroleum and shale petroleum oils, but it furnished the best means available of testing the analytical methods, and the results are of value if properly interpreted. Both concentrated and dilute hydrochloric acid dissolved part of the amylene and gave high results for the amount of nitrogen compounds present. In the run in which 10 per cent hydrochloric acid was allowed to stand with the test solution overnight the result was the same as that determined with concentrated sulfuric acid, indicating solution in the acid of all the amylene and pyridine. However, other tests with well petroleum gasoline and hydrochloric acid did not show appreciable solution of the unsaturates, although 26 per cent acid colored the gasoline light brown in a few minutes indicating some reaction. The discrepancy between these results is probably due to the greater activity of the amylene as compared to the unsaturated compounds actually present in gasoline.

A series of experiments was run to determine the approximate solubility and rate of solution of such nitrogen bases as pyridine and quinoline with acetic and hydrochloric acids. The hydrochloric acid dissolved quinoline but slowly, leaving an undissolved residue at the end of 30 minutes. In glacial acetic acid these bases instantly dissolved and were not precipitated out upon dilution with water; indicating strongly the superiority of this reagent for determining the nitrogen bases present in shale oil distillates. Accordingly, the method was devised and tested with various solutions. The glacial acid was first added to the oil and afterwards diluted with water to insure more intimate contact. Part of the saturated and unsaturated hydrocarbons dissolve in the acid, but are precipitated out upon dilution with water.

Well petroleum gasoline, free from nitrogen bases, showed no compounds absorbed by 15 per cent acetic acid and did show slight absorption by hydrochloric acid. This same gasoline analyzed 12 per cent unsaturates by the sulfuric acid method.

In test solutions of this gasoline to which had been added known amounts of pyridine and quinoline, sulfuric acid completely absorbed both nitrogen and unsaturated compounds, whereas hydrochloric and acetic acids absorbed only the former.

A test of the gasoline solution of quinoline after washing with sulfuric acid gave no indication of nitrogen compounds with 25 per cent acetic acid, proving that they were completely absorbed by the sulfuric acid.

Samples of shale-petroleum distillates analyzed for nitrogen bases both with hydrochloric acid and 25 per cent acetic acid gave results 1 to 2 per cent higher with the acetic acid and the solutions were clearer and easier to read. It was found that 4 per cent hydrochloric acid completely dissolved, though but slowly, a nitrogen base such as quinoline, but undoubtedly a higher concentration than this should be used in view of the higher molecular-weight nitrogen compounds present in the shale distillates. As 26 per cent hydrochloric acid reacts slightly with the unsaturates, a concentration intermediate between these two of approximately 15 per cent was considered best.

Conclusion

From the results obtained it is evident that 25 per cent acetic acid is the best reagent to use for a rapid determination of the nitrogen bases in petroleum distillate. It gives clearer solutions, dissolves more of the nitrogen compounds, dissolves them more quickly, and causes less polymerization than hydrochloric acid.

New Institute of Cellulose at McGill University—The corner stone of the new Institute of Cellulose, which is being constructed by the Canadian Pulp and Paper Association on the McGill Campus, in Montreal, has recently been laid. Fundamental scientific and industrial research on cellulose technology will be conducted jointly by McGill University, the Canadian Pulp and Paper Association, and the Dominion Government.

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[5] *Bur. Mines, Tech. Paper* **181** (1917).

Protective Tubes for Thermocouples for Determining Heat Penetration in Processed Foods[1]

By K. L. Ford and A. G. Osborne

Glass Container Association, 22 East 75th St., New York, N. Y.

In the determination of temperature changes within food containers during processing the use of Bakelite as a protective tube for the thermocouple eliminates one important source of error, the flow of heat along the tube. This error in heat-penetration determinations has been the subject of much discussion, but apparently only the respective merits of glass and metal tubings have been considered. The former requires careful handling, whereas the latter, owing to its high heat conductivity, introduces an error into the determination of the temperature changes. In this laboratory extensive experience has demonstrated that Bakelite makes an ideal substitute for glass or metal tubing, for it possesses a lower heat conductivity than metal and greater resistance to failure than glass.

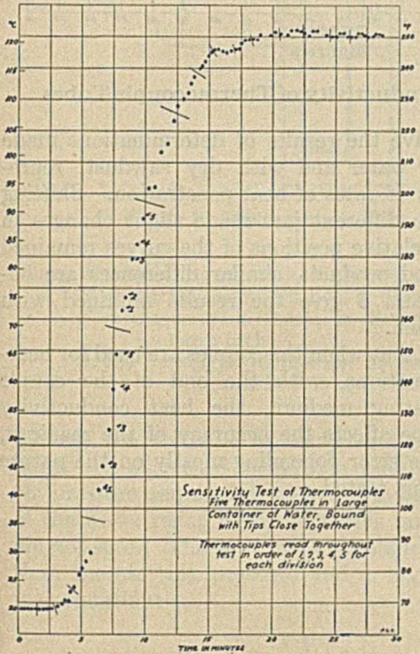

Figure 1

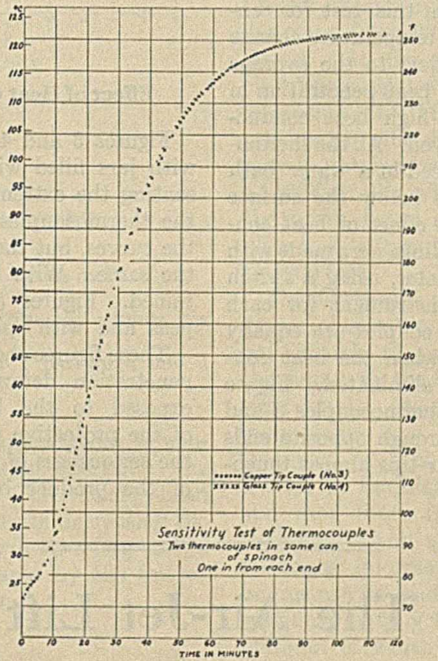

Figure 2

The purpose of this paper is to point out the possibilities of error due to heat conductivity down the metal tube and illustrate briefly the results obtained when using various types of protective tubes for thermocouples.

Protective Tubes Tested

Five types of thermocouple-protecting tubes were selected as representative of the essential differences which might affect the accuracy of temperature determinations in heat-penetration studies:

No. 1—The upper section is a brass tube $^5/_{16}$ inch in diameter with a $^1/_{32}$-inch wall at the end of which is soldered the copper wire of the couple. A copper tube $^3/_{16}$ inch in diameter with the constantan wire soldered into the end is soldered into the brass tube.

No. 2—The brass tube forming the upper section is $^3/_{16}$ inch in diameter with $^1/_{32}$-inch wall. Soldered into this is a copper tube 0.1 inch in diameter with 0.01-inch wall with the couple junction sealed in the end with solder.

No. 3—The tube is Bakelite $^1/_4$ inch in diameter with $^1/_{16}$-inch wall. The couple junction is sealed into a short piece of copper tubing 0.1 inch in diameter with 0.01-inch wall with solder and the copper tube secured in the Bakelite tube with cement.

No. 4—This couple tube is the same as No. 3, except that the couple junction is coated with glass which is cemented into the end of the Bakelite tube.

No. 5—The tube is Bakelite $^3/_8$ inch in diameter with $^1/_8$-inch wall. The couple junction is secured to a copper tip by solder which is screwed into the end of the tube.

Nos. 1 and 2 were exact duplicates of thermocouples employed by former investigators. Nos. 3 and 4 have been used in this laboratory. No. 5 was designed by the authors for special service where rugged construction was more essential than high sensitivity.

It is apparent from the construction of these thermocouples that there are differences in sensitivity and ability to indicate correct temperature changes under varying conditions. Considerable differences in mass and thermal conductivity exist, which must necessarily affect the sensitivity. The pronounced difference in thermal conductivity between the Bakelite and copper may be

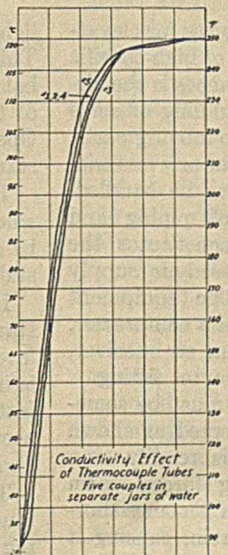

Figure 3

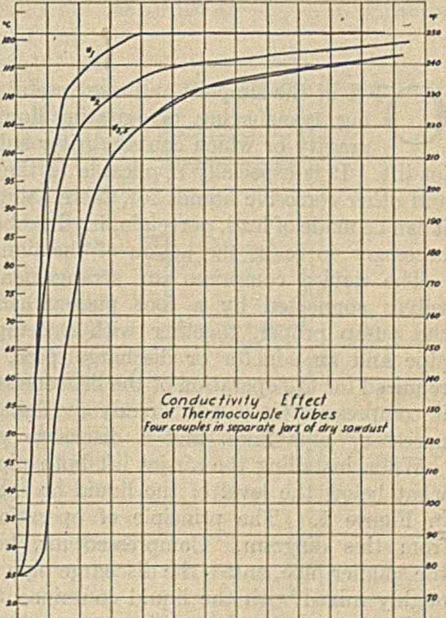

Figure 4

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[1] Received April 19, 1927.

a factor of some importance. The actual influence of these factors depends upon the rate of temperature change and the medium in which the temperature is determined. The work in this laboratory has brought out several other factors of seemingly negligible importance which exert an appreciable influence on the observed readings. These factors have been considered in the construction of the Bakelite tube couples.

Sensitivity of Thermocouples

Numerous methods might be employed to check the relative sensitivity of the thermocouples, but owing to the differences in the rate of temperature changes and in the bath medium employed for the checking, the results might be misleading in demonstrating the practicability of the thermocouples for heat-penetration service. In this test for sensitivity a rate of temperature change approximately equal to the average over-all rate for heat penetration in material having high heat conductivity was employed. All the thermocouples were placed in a water bath with their tubes below the surface to eliminate the effect of heat conduction along the tubes. The e. m. f. readings were made with a Leeds & Northrup Type K potentiometer, using a switch to connect one thermocouple to the instrument for each reading. Figure 1 shows that the five couples are equally sensitive, as they show no differences when the heat conductivity effect of the protective tube is eliminated. Figure 2 shows the results obtained by using thermocouples 3 and 4, having the thermocouples inserted through opposite ends of a can of finely cut spinach, with their tips almost touching.

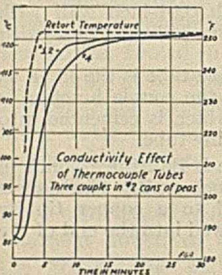

Figure 5

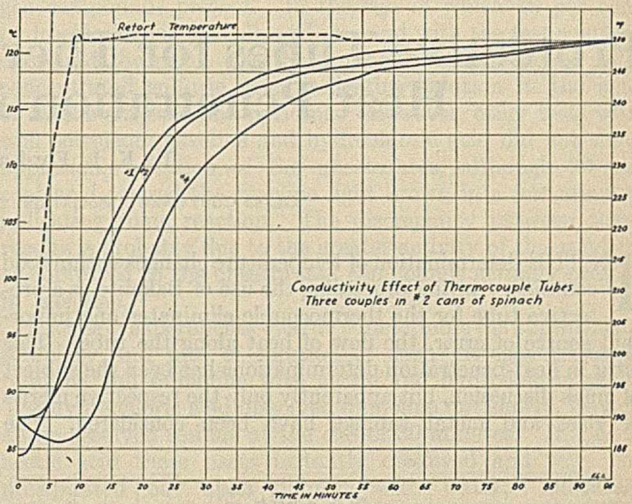

Figure 6

Effect of Heat Conductivity of Thermocouple Tubes

Figures 3 and 4 give the results of determinations made with jars filled with water and with dry sawdust, representing the extremes of rates of heat penetration. Shifting the thermocouples to different jars made slight changes in the curves, but the relative positions of the curves remained the same. With food products, similar differences are obtained. Figures 5 and 6 give the results obtained with peas and with spinach.

These figures show that when the couples are used for heat-penetration determinations, with the end of the couple exposed to the heating medium, the heat conductivity of the protective tube affects the accuracy of the readings, the seriousness of the error depending mostly on the nature of the product being tested.

The Air-Jet Lift[1]

By S. C. Martin

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ONE of the simplest and most useful devices for elevating, transferring, or agitating liquids of high specific gravity or which contain gritty substances is the air-jet lift. It is especially applicable to the handling of acids and other corrosive liquids for, there being no moving parts, it can be made of lead, porcelain, hard rubber, or any material necessary to resist the action of the liquid to be handled.

The device comprises an arrangement of piping and valves connected by a foot piece which constitutes the the pump proper, together with a compressed-air supply pipe and an eductor or discharge pipe. The equipment required for the operation of the lift consists of a compressor, if compressed air is not already available, an air receiver, necessary pipe lines, and a discharge piece or fitting.

When installing the air-jet lift both pipes must be somewhat below the level of the liquid or submerged as shown in Figure 1. The principle of operation is readily seen from this diagram. Compressed air, being forced down the smaller pipe, enters the discharge pipe and becomes thoroughly mixed with the liquid contained therein, causing it to become an emulsion of water and air, and therefore lighter than the water surrounding the discharge pipe. This lighter mixture rises and tends to restore the hydrostatic balance, its upward movement being assisted by the motion of the compressed air as it expands in the discharge pipe. Opening a valve in the compressed-air line is sufficient to start or stop the operation of the lift.

The foot piece or pump consists of a nozzle in a chamber wherein the air is thoroughly mixed with the liquid, a strainer being provided at the bottom when the device is to be installed in a well.

It will be noted that there are two submergences, the starting submergence and the operating submergence, the level of the liquid in the well being lowered when the lift is in operation. The proper submergence for any particular installation depends upon several factors and cannot be accurately determined unless the conditions of service are known.

The air pressure necessary to start the lift can be easily found by means of the following formula, when the starting submergence and the losses in the air line are known:

$$P = S \times 0.434 + F \qquad (1)$$

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[1] Received July 2, 1927.

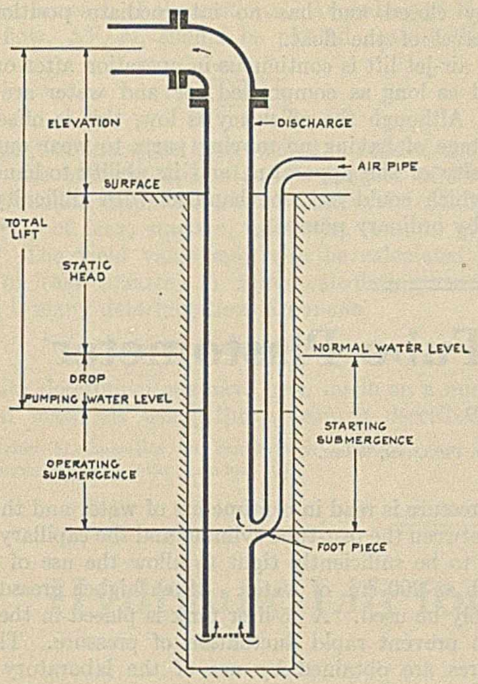

Figure 1—Diagrammatic View of Air-Jet Lift

where P = starting pressure, in pounds per square inch
S = starting submergence, in feet
F = transmission losses in the air line, in pounds per square inch
0.434 = weight of column of water 1 foot high and 1 square inch in cross section

Since the water level falls and the submergence is consequently decreased while the pump is in operation, the air pressure required is also decreased. The velocity head of the water rising in the pipe aids further in decreasing the air pressure. The working air pressure will therefore be less than the starting pressure and is expressed by the following equation:

$$P = \left(S - \frac{V}{2g}\right) 0.434 + F \qquad (2)$$

where P = working pressure, in pounds per square inch
S = the operating submergence, in feet
V = water velocity, in feet per second
g = 32.16 feet per second
F = transmission losses in the air line, in pounds per square inch

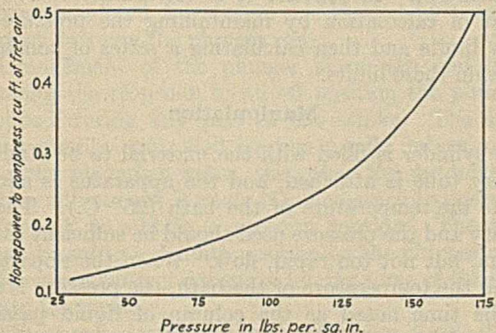

Figure 2

If the total lift is known, the quantity of free air required to raise the liquid may be determined approximately by the equation:

$$A = \frac{WL}{20} \qquad (3)$$

where A = quantity of free atmospheric air under standard conditions, in cubic feet per minute
W = quantity of water, in cubic feet per minute
L = total lift above surface of water, in feet

The power required to compress 1 cubic foot of free air to different gage pressures per square inch may be determined from Figure 2. This curve was plotted from actual practice and takes into consideration the various losses in the air cylinder, heat, friction, etc.

The over-all efficiency of the air-jet lift or the ratio of the water horsepower to the indicated horsepower of the compressor steam cylinder runs from 20 to 60 per cent, the efficiency decreasing with increasing lift. Fifty per cent efficiency may be obtained with a 100-foot lift while the lower figure applies to lifts from 900 to 1000 feet.

Should the submergence obtainable be not enough to raise the liquid to the desired height, two or more stages may be arranged—that is, the liquid may be pumped into a tank located at the highest point to which it can be first raised and then lifted from this tank to a greater height.

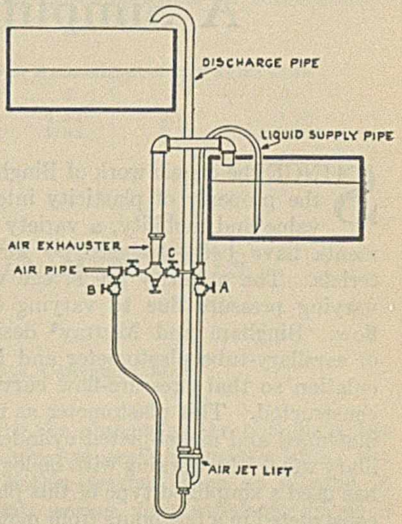

Figure 3—Arrangement Used to Elevate Acid

In figuring on an air lift for any specific installation, the following information should be obtained before calculations can be made: temperature of the liquid to be raised, specific gravity of the liquid, kind of solution to be pumped, material of which the pump is to be made, quantity of liquid to be handled, submergence, and lift.

Various applications of the air lift are shown in the accompanying cuts. Figure 3 shows an arrangement used for elevating commercial sulfuric acid. Here a siphon is employed to carry the liquid to the air-jet lift. In starting this apparatus the valves A and B are closed and air is forced into the top of the vessel. The valve C is now opened, making communication between the siphon pipe and the air exhauster and a suction created in the supply pipe by the exhauster, drawing in liquid and forcing it with the compressed air back into the top of the tank. As soon as the circulation is well established the valves A and B are opened and the other valves closed, when the liquid will continue to

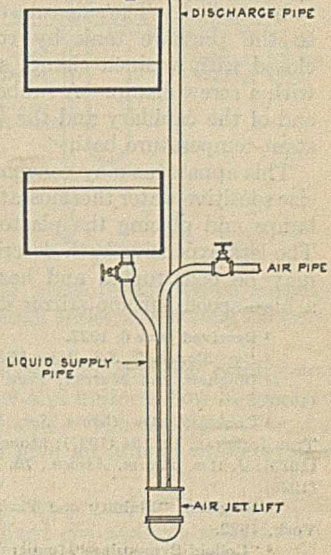

Figure 4—Transferring Solutions with Air-Jet Lift

flow through the siphon and the supply pipe to the lift, from which it is forced into the tank above.

A solution is easily transferred from one vessel to another as shown in Figure 4, and the arrangement may be used for various purposes. By a similar device an air-jet compressor may be made to supply the compressed air.

Automatic control may be applied to the lift by employing a float to operate a snap valve in the compressed-air line. This type of valve remains either entirely open or entirely closed and has no intermediate position during the travel of the float.

The air-jet lift is continuous in operation after once being started as long as compressed air and water are supplied to it. Although the efficiency is low, this is offset by the advantage of having no moving parts to wear out, by the simplicity of the apparatus, and its ability to handle materials which could only be handled with difficulty or not at all by ordinary pumps.

A Simplified Capillary-Tube Plastometer[1]

By J. L. St. John

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SINCE the classic work of Bingham,[2] in which he resolved the property of plasticity into two components, yield value and mobility, a variety of capillary-tube instruments have been designed[3,4,5] for use with different materials. The majority are of the vertical type involving a varying pressure due to varying hydrostatic head during flow. Bingham and Murray[3] designed a horizontal type of capillary-tube plastometer and Kelly[6] simplified the calculation so that pressure-flow curves might be more easily constructed. This plastometer as used by Kelly required a machined and nickel-plated cylinder and guard for the capillary tube. In working with biological materials, the author has used a simplified type of this plastometer, which may be constructed in a few hours from materials found in any laboratory at a negligible cost.

Description

The cylinder is made from an ordinary 125 by 16-mm. soft-glass test tube, cut to a length of about 70 mm. and relipped. A side tube of soft-glass tubing 5 mm. in diameter and about 60 mm. long is blown into the shortened test tube as near the bottom as is convenient (10 to 15 mm.). Other sizes of test tubes may be used depending on the requirements of the work. A length (76.5 cm.) of heavy-wall capillary tubing (7 mm. external diameter), with the desired internal diameter, is inserted into a No. 0 rubber stopper cut to a length of about 1 cm. This stopper is securely inserted into the test tube after it has been filled with the material to be studied. The side tube of the cylinder is then connected to the pressure tank by rubber tubing. The tubing is closed with a pinch clamp, sometimes used in conjunction with a screw clamp. A rubber tube is connected to the exit end of the capillary and the apparatus is placed in the constant-temperature bath.

This apparatus may conveniently be used in a Freas large-size sensitive water thermostat by removing one of the heating lamps and placing the plastometer cornerwise in the bath. The less expensive bath described by Bingham and Murray[3] may be constructed and heated with knife heaters, using a high-speed turbine stirrer and a Harvey thermoregulator. The pressure is read in centimeters of water and the connection between the test-tube cylinder and the capillary has been found to be sufficiently tight to allow the use of pressures as high as 200 cm. of water. Much higher pressures could probably be used. A 15-liter tank is placed in the pressure line to prevent rapid fluctuation of pressure. The higher pressures are obtained by use of the laboratory pressure system.

Calibration of Capillary Tube

The capillary tube is accurately laid off in 10-cm. sections with a Vernier caliper beginning at the end inserted into the rubber stopper, the divisions being marked with a file or diamond point. The visibility of the division lines may be increased with a thin line of black paint. Small strips of gummed labels may be pasted opposite the marks on the tube to facilitate observation. Thermometer tubing may also be used in place of regular capillary tubing.

In calibrating the tube, mercury is drawn into it in amount sufficient to fill the capillary for a little over 10 cm. The exact length of this mercury column is determined in each 10-cm. section of the tube. The mercury is then weighed and its volume calculated. From these data the volume, ΔV, and the average radius of each section of the tube are calculated. Using Kelly's formula

$$\frac{\pi R^4 gP}{8\left(\frac{l_2 + l_1}{2}\right)}$$

a constant is calculated for each section of the tube, which includes all of this formula except the value for P. This constant is then multiplied by the observed pressure for each determination. In practice it is convenient to reduce the amount of calculation by maintaining the pressure within narrow limits and then calculating a series of_constants for use within these limits.

Manipulation

The cylinder is filled with the material to be studied, the capillary tube is attached, and the apparatus is allowed to come to the temperature of the bath (25° C.). The size of capillary and the pressure used should be sufficient to cause a uniform, but not too rapid, flow. When the apparatus has reached the temperature of the bath, the pressure is released and the time noted as the column of liquid passes each division of the capillary tube. Zero time may be taken at the first division where the flow is not too rapid to permit accurate timing. A split-second stop watch is necessary for this.

From the stop-watch readings the time of flow, Δt, for each division is determined. From this value and the volume of each division of the tube, ΔV, the rate of flow $\Delta V/\Delta t$ is

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[1] Received June 6, 1927.

[2] *Bur. Standards, Sci. Paper* **278** (1916).

[3] Bingham and Murray, *Proc. Am. Soc. Testing Materials*, **23**, 655 (1923).

[4] Cooke, *J. Am. Ceram. Soc.*, **7**, 651 (1924); Herschel and Bulkley, THIS JOURNAL, **19**, 134 (1927); Moness and Giesy, *J. Phys. Chem.*, **29**, 1282 (1925); *J. Am. Pharm. Assocn.*, **15**, 39 (1926); Sharp, *Cereal Chem.*, **3**, 40 (1926).

[5] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922.

[6] "Colloid Symposium Monograph," Vol. III, p. 303, Chemical Catalog Co., New York, 1925.

calculated for each of the sections. According to Kelly the rate of flow, $\Delta V/\Delta t$, should be plotted against the value

$$\frac{\pi R^4 g P}{8\left(\frac{l_2+l_1}{2}\right)}$$

The tangent of the angle thus formed is defined as the mobility of the material studied. The tangent of the angle may be obtained graphically, but is preferably calculated by the method of least squares, using the formula given by Mellor.[7] The yield value may also be calculated by the method of least squares. A rapid calculating machine is essential if many determinations are made.

Mobility Determinations

Mobility determinations have been made on a number of biological materials using the apparatus described. The results obtained with this instrument are compared with those obtained with the Bingham and Murray plastometer in Table I, which gives data obtained on duplicate flour-in-water suspensions prepared by mixing 30 grams of flour and 70 cc. of water and gently working in a mortar, a small portion at a time.

Table I—Mobility of Flour-Water Suspensions

Flour No.	Simplified Plastometer 1	2	3	Av.	Bingham-Murray Plastometer 1	2	3	Av.
1	0.759	0.714	0.780	0.751	0.731	0.742	0.777	0.750
2	0.593	0.648	0.688	0.643	0.667	0.793	0.693	0.718
3	0.732	0.761		0.747	0.740	0.755		0.747

Table II gives mobility determinations on reconstituted dry-skim milk.

Table II—Mobility of Reconstituted Dry Skim Milk

Milk	1	2	3	Av.
1	0.51	0.50	0.56	0.52
2	1.95	1.85	1.71	1.84

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[7] "Higher Mathematics for Students of Chemistry and Physics," p. 326, Longmans Green & Co., London, 1916.

Hydraulic Lift for Gas Analysis Apparatus[1]

By E. J. Tauch

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

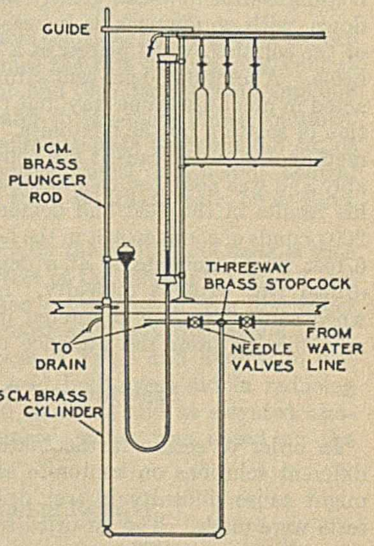
A SIMPLE and flexible device for mechanically raising and lowering the mercury bulb of a gas analysis apparatus, or other apparatus in which mercury is used for displacement, is shown in the accompanying diagram. It is especially useful where a large number of analyses must be made, or where the operator must give most of his time to the control of other apparatus. The only attention required is an occasional shift of a stopcock lever and the leveling and reading of the mercury level between absorptions.

Water pressure supplies the operating power, raising and lowering a plunger which carries the bulb support. With the three-way stopcock in one position, water flows into the cylinder and raises the plunger until the overflow pipe is reached. During this up-stroke the gas to be analyzed has been forced into one of the pipets. It will remain here until the three-way stopcock is shifted to the other position. The weight of the plunger and the mercury now forces the water out of the cylinder and into a drain, the gas being drawn back into the buret at the same time. This operation is repeated as many times as is desired by merely shifting the stopcock lever back and forth. When the absorption has been completed the mercury is leveled by moving the bulb up or down on the plunger rod.

The movement of the plunger is smooth and uniform. By moving the stopcock to an off position the plunger can be stopped during any part of the stroke. The speed of travel is readily controlled by two needle valves, one controlling the incoming water, the other the outgoing water. Once this adjustment is made it is necessary to operate only the stopcock to obtain a uniform motion. The mercury bulb can be set to a definite position on the plunger rod such that there is never any danger of forcing some of the mercury over into the pipets.

The brass cylinder should be about 2.5 cm. inside diameter. Its length will be determined by the length of the buret with which the apparatus is to be used. An additional allowance of about 15 cm. should be made for connections. A plunger rod about 1 cm. in diameter is sufficiently rigid. Its length should be such that, with the plunger at the bottom of the cylinder, the rod will project several centimeters above the guide. A cup-shaped leather washer, such as is used in an automobile tire pump, serves very satisfactorily as a plunger.

If desired, the device can be made entirely automatic in operation, with the exception of leveling and reading. A simple mechanism for shifting the stopcock lever at the end of each stroke, either mechanically or electrically, can be constructed for this purpose.



The hydraulic lift not only eliminates the work of raising and lowering the heavy mercury bulb, but it also gives more accurate results in analysis because of more consistent operation. There is always a tendency to raise and lower the bulb too rapidly when this must be done by hand. The resulting irregular pressure differences increase the error resulting from any small leaks which may be present in the apparatus.

The lift is particularly useful in making combustion analyses, in which a very slow and uniform flow of gas into the combustion pipet is desirable. The needle valves, for this use, can be adjusted to give an almost imperceptible motion of the plunger.

Its performance in practice has proved so successful that it has been installed on all fixed gas analysis apparatus in this laboratory.

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[1] Received June 16, 1927.

The Swelling of Bentonite and Its Control[1]

By C. W. Davis

Rare and Precious Metals Experiment Station, in Coöperation with the University of Nevada, Reno, Nev.

A study of the effect of different liquids on the swelling of bentonites shows that lubricating oil, kerosene, and gasoline prevent swelling and leave a hard, granular residue and that, while dilute solutions of various salt solutions retard swelling, saturated solutions of specific salts are required to obtain the maximum effect, with a resultant firm residue, for each type of bentonite.

Change of temperature from 1° C. to 94° C. accelerates the rate of swelling but has little effect on the final volume for the solutions used. Increase of acidity or alkalinity depresses the swelling of bentonite. Equivalent quantities of neutral salts reduce the swelling of bentonite to about the same degree but univalent anions are slightly more effective than polyvalent anions.

The specific dehydration effect of several cations at certain given normalities, although small, follows the same order for chlorides and sulfates.

IN DRILLING wells while searching for oil, potash, or other minerals, water is generally used. If bentonite is encountered the drilling water causes the bentonite to swell and form a sticky mass which flows into the hole. As more water becomes mixed in, the mass becomes less viscous and finally results in a permanent suspension. There is a continuous transition from the stiffest paste to the most mobile suspension, all dilutions being capable of holding other minerals in suspension. If oil is present bentonite promotes the formation of water-oil emulsions, which may be very viscous or practically solid. In any case bailing is very difficult and tedious. The sides of the hole may swell, heave, and cave, and may result in casing collapse. It is therefore evident that the prevention of the swelling of bentonite encountered in drilling is an important problem.

Warren[2] in a few qualitative experiments found that a bentonite which swelled greatly when placed in water broke down, with no appreciable increase in volume or absorption of the solution, when placed in a saturated sodium chloride brine. A solution 50 per cent saturated with sodium chloride acted in much the same way, but there was a greater absorption of solution by the bentonite. A 25 per cent solution of methanol in water caused the bentonite to expand considerably and was absorbed to a notable extent. Warren applied his results in the field and demonstrated that by dumping 200 pounds of common salt in the hole, a bed of pure bentonite 6 feet thick encountered at a depth of 1895 feet could be drilled wet without difficulty. He also pointed out that when salt water is encountered in drilling there should be no difficulty from the presence of bentonite.

Experimental Procedure

In order to secure further data concerning the effect of different solutions on bentonite and clay-like material that might cause difficulty in wet drilling, about five hundred tests were made. The air-dried samples were stage-crushed through 10 mesh. The apparent volume of 2.5 grams was measured, and this sample passed slowly through a funnel into a test tube containing about 20 cc. of the solution being tested. After 24 hours the height of the swelled sample was marked on the test tube; the appearance and feel of the material were noted, the tube was washed clean, and the volume occupied by the swelled sample measured by observing the quantity of water run from a buret that filled the tube to the mark.

Types of Volume Increase

Preliminary experiments indicated two pertinent types of apparent volume increase. The first type is due to the breaking down of granules into a state of finer division when placed in a liquid. Material which exhibited none of the properties of bentonite gave this effect. For example, when a 2.5-gram sample having an apparent volume of 2.4 cc. at −10 mesh was pulverized in a mortar to −200 mesh, its apparent volume became 4.9 cc., and when 2.5 grams of the −10-mesh sample were placed in water, it broke down giving an apparent volume of 5.2 cc. Although this breaking-down effect was considerably decreased in saturated solutions of several salts, of the liquids tried, only gasoline, kerosene, and lubricating oil had no visible effect (except to change the color) on the clays and bentonites. In these liquids the solids retained their original hard, granular characters and the resultant volumes were the same as the apparent volume of the dried samples of the same fineness.

The second type of expansion is a real swelling. In water it is very marked for typical bentonite, being up to about seven times the original apparent volume and about eighteen times the actual volume of the bentonite dried at 105° C. (average specific gravity 2.75).

Effect of Addition of Salt Solutions

Table I gives a few typical results showing the volumes of different bentonites and clays resulting from the addition of solutions that might be used commercially to aid in wet drilling.

These tests and others show that the addition of small quantities of any one of a number of soluble salts (up to about 2 per cent) markedly decreases the swelling produced when bentonites are treated with water. The additional retarding effect becomes less as the salt solution becomes more saturated.

Combinations of various salts resulted in the volume increase that would be expected from a consideration of the action of the single salts, no abnormal action being encountered.

Soaked bentonite residues from the more dilute solutions were not visibly granular and felt smooth when rubbed between the fingers, but as the salt concentration became greater the residues became visibly granular although still soft. As the solutions became saturated all residues were visibly granular and many remained hard, resembling the original, dry, crushed material. The firmness of clay and bentonite residues (except those from substances that are not affected by water) seems to be a function of the nature of the solution

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[1] Received May 24, 1927. Published with permission of the Director of the U. S. Bureau of Mines. Not subject to copyright.

[2] *Mining Met.*, **7**, 349 (1926).

and of the material, and the degree of this hardness follows approximately in reverse order the apparent volume of the soaked residue, regardless of the solution used; that is, the smaller the resulting solid the harder it is. This may be exemplified by the action of different reagents upon a typical bentonite whose apparent dry volume of 2.3 cc. became 16 cc. when placed in water. This material as well as all other samples of clay or bentonite tested, when soaked in gasoline, kerosene, or lubricating oil produced a very hard, harsh, firm residue, and there was no visible evidence of disintegration or increase of volume after several days' treatment. A saturated solution of lithium chloride gave a very hard residue with an apparent volume of 2.6 cc. The residues became successively softer and more voluminous in saturated solutions of the following salts: LiCl, NH_4Cl, $(NH_4)_2SO_4$, $FeCl_3$, KCl, Na_2CO_3, NaCl, $MgSO_4$, $MgCl_2$, $SrCl_2$, $AlCl_3$, $CaCl_2$, $BaCl_2$, $Al_2(SO_4)_3$, 95 per cent C_2H_5OH, Na_2SO_4, and $CaSO_4$.

Table I—Apparent Volume Occupied by Bentonites and Clays when 2.5 Grams Were in Contact with Different Solutions for 24 Hours at 20° C.[a]

(Figures in cubic centimeters)

SOLUTION	No. 1	No. 9	No. 11	No. 14	No. 15	No. 16	No. 17	No. 18
Dry	2.0	2.4	2.0	3.2	2.3	2.3	2.3	2.9
Water	10.0	7.5	13.5	5.8	9.5	15.0	6.7	12.6
Sodium chloride:								
0.5%	8.0	7.2	11.2	5.5	7.1	11.5	6.7	8.1
2%	5.5	6.5	6.6	5.3	6.3	6.5	6.1	6.7
10%	4.4	5.8	3.9	5.1	5.4	4.3	5.1	4.9
Saturated	3.8	5.2	3.7	5.0	4.8	3.8	4.4	4.5
Potassium chloride:								
0.5%	7.1	6.7	12.2	5.5	6.6	11.1	6.0	7.6
2%	4.8	6.5	5.3	5.2	6.0	4.8	5.8	6.2
10%	4.3	5.5	3.7	5.0	5.2	3.2	4.9	4.9
Saturated	3.4	4.8	3.5	4.7	4.6	3.2	4.4	4.4
Magnesium chloride:								
0.5%	6.2		6.0		6.8	8.7		6.9
2%	5.2		5.8		6.5	6.1		6.5
10%	4.7		4.9		5.4	4.6		6.5
Saturated	4.6		4.0		4.4	3.9		4.5
Sodium sulfate:								
0.5%	7.6				7.9	14.8		
2%	6.0				6.8	8.5		
10%	4.8				5.4	5.7		
Saturated	4.8				4.7	4.1		
Potassium sulfate:								
0.5%	7.5				7.1	13.0		
2%	5.6				6.4	7.0		
10%	4.3				5.4	4.4		
Saturated	3.9				4.7	4.4		
Magnesium sulfate:								
0.5%	6.9		8.0		7.0	9.2		6.8
2%	5.3		6.6		6.4	6.6		6.6
10%	4.2		5.3		5.2	5.2		5.8
Saturated	3.7		3.7		4.2	3.8		5.6

No. 1—Bentonite from near Fallon, Nev. (similar to Wyoming type bentonite).

No. 9—"Otaylite" from Otay, Calif.

No. 11—Bentonite from near Belle Fourche, S. D. (similar to Wyoming type).

No. 14—"Shoshonite" from Shoshone, Calif.

No. 15—"Oil filtering clay" from Nye County, Nev.

No. 16—Bentonite from Medicine Bow, Wyo. (similar to Wyoming type).

No. 17—Bentonite from north of Santa Fe, N. M.

No. 18—Bentonite from near Randsburg, Calif. (similar to Wyoming type).

[a] The results are probably accurate to within 0.5 cc.

Effect of Temperature and H-Ion Concentration

Two factors which are known to have considerable effect on the swelling of gels, temperature and hydrogen-ion concentration, were studied in their relation to the swelling of a typical bentonite (No. 16 in Table I). The results are given in Table II.

Increase in temperature seems to promote swelling, but the small effects shown in the table may well be due to increased rate of swelling (so that readings may have been taken before the maximum volume was reached) rather than to an ultimate difference in volume.

Increased acidity or alkalinity caused a reduction of swelling, but the retardation was small near the neutral point where many salt solutions have a large effect.

Table II—Effect of Temperature and Hydrogen-Ion Concentration on the Swelling of Bentonite

SOLUTION	pH	VOLUME OF 2.5 GRAMS AT DIFFERENT TEMPERATURES 1° C.	20° C.	45° C.	94° C.
		Cc.	*Cc.*	*Cc.*	*Cc.*
HCl	0.1	..	5.5	..	..
HCl	1	11.1	11.7	12.3	13.1
HCl	2	..	13.5	..	..
HCl	3	..	14.5	..	..
HCl	4	..	14.8	..	..
HCl	5	..	15.0	..	..
H_2O	6	14.3	15.0	15.4	15.6
NaOH	7	..	14.8	..	..
NaOH	8	..	14.8	..	..
NaOH	9	..	14.7	..	..
NaOH	10	..	14 6	..	..
NaOH	11	..	14.4	..	..
NaOH	12	..	14.2	..	..
NaOH	13	11.2	12.0	13.2	13.1
NaOH	14	..	6.6	..	..
NaCl (0.1 *N*)	6	11.2	11.5	12.0	12.5
NaCl (*N*)	6	4.3	4.5	4.8	5.1
NaCl (satd.)	6	3.8	3.8	3.6	3.7

Effect of Equivalent Concentrations of Different Salts

To determine the relative effect of different salts in solutions of equivalent concentrations, the experiments whose results are given in Table III were performed, using a bentonite from near Newcastle, Wyo.

Table III—Apparent Volume Occupied by Typical Bentonite when 2.5-Gram Samples Were Left in Contact with Equivalent Quantities of Different Solutions for 24 Hours at 20° C.

(Dry volume 2.3 cc., volume in water 16 cc.)

REAGENT	0.5 NORMAL	NORMAL	3 NORMAL
	Cc.	*Cc.*	*Cc.*
LiCl	...	...	4.2
NaCl	7.4	4.4	3.9
KCl	5.2	3.8	3.6
NH_4Cl	6.0	4.0	3.8
$MgCl_2$	7.3	5.0	4.2
$CaCl_2$	6.4	4.8	4.1
$SrCl_2$	6.0	4.9	4.1
$BaCl_2$	6.4	4.9	4.2
$FeCl_3$	5.9	4.2	3.6
Al_2Cl_6	5.8	4.2	3.7
Na_2SO_4	10.0	5.1	4.1
K_2SO_4	7.0	4.1	...
$(NH_4)_2SO_4$	6.2	4.6	4.0
$MgSO_4$	7.3	5.4	4.2
$FeSO_4$	6.3	4.3	3.6
$Al_2(SO_4)_3$	6.4	4.1	3.6
Na_2CO_3	6.2	5.6	4.0

The results for the 0.5 normal solutions have a greater chance for error than the others, since the rate of change of volume with change of concentration and the effect of small amounts of soluble impurities is greater in the more dilute solutions.

As the method gives results accurate to about 0.5 cc., it is seen that equivalent concentrations of different neutral salts cause very nearly the same retardation in the swelling of bentonite.

The prevention of swelling by the addition of salts is thus largely dependent on the effect of the salt concentration and on the resulting hydrogen-ion concentration, the first effect being more important for most salts but the second effect becoming evident in the case of ferric and aluminum sulfates and chlorides whose acid hydrolyses aid in reducing the swelling. (In saturated solutions and at elevated temperatures considerable chemical action was noted on the addition of these salts.)

Discussion of Results

Many substances swell when placed in a suitable liquid. This action has been studied by a large number of investigators.[3] The more important theories that have been pro-

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[3] Wilson, *J. Chem. Soc.*, **109**, 307 (1916); *J. Am. Leather Chem. Assocn.*, **12**, 108 (1917); "The Chemistry of Leather Manufacture," 1923; J. A. and W. H. Wilson, *J. Am. Chem. Soc.*, **40**, 886 (1918); Procter, *J. Chem. Soc. (London)*, **105**, 313 (1914); Procter and Wilson, *Ibid.*, **109**, 307 (1916); Loeb, "Proteins and the Theory of Colloidal Behavior," 1922; *J. Gen. Physiol.*, **1**, 41 (1918); Procter and Burton, *J. Soc. Chem. Ind.*, **35**, 404 (1916); Fischer, *Science*, **42**, 223 (1915); "Soaps and Proteins," p. 222 (1921); Pfeffer and de Vries, "Pflanzen Physiol.," Leipzig, Vol. I, p. 116 (1897); Overton, *Z. physik. Chem.*, **22**, 189 (1897); Tolman, *J. Am. Chem. Soc.*, **40**, 246 (1918); Lloyd, *Biochem. J.*, **14**, 147 (1920); Katz, *Z. physiol. Chem.* **96**, 255 (1916); Bartell and Sims, *J. Am. Chem. Soc.*, **44**, 289 (1922).

posed to account for it have been discussed by Bartell and Sims,[4] who list them under the following titles: "(*a*) capillary theory, (*b*) osmotic theory, (*c*) lipoid membrane theory, (*d*) colloid chemical theory, (*e*) repulsion theory, (*f*) diffusion theory, and (*g*) solid solution theory." They suggest that all these concepts, together with others such as the principles underlying anomalous osmose, are necessary to form a satisfactory explanation that will cover all cases. Swelling, whatever its mechanism, is an increase in volume due to the taking up of a liquid.

An understanding of the swelling of crude bentonite is complicated by the facts that the material is not a pure substance; that it has no definite chemical composition; that its composition may change in the presence of salt solutions; and that it frequently contains varying amounts of soluble salts.

Temperature, hydrogen-ion concentration, and the presence of soluble salts are known to have an important effect on the swelling of gelatin, proteins, and other substances.

Fulmer[5] has pointed out that the effect of various salts on the swelling of gels may depend on the temperature in such a way that the arrangement of salts in order of their suppression of swelling (their dehydration power) for one temperature would not necessarily hold for another. The swelling of bentonite, however, as has been shown, is but little changed by temperatures between 1° and 94° C., but with certain solutions there might be considerable difference due to increased ionization of the salts and accelerated chemical reaction.

The addition of acid or alkali decreases the swelling power of bentonite in water, but this effect is very small in the range pH 4 to 9.

The measurable effect of neutral salts on swelling seems to depend somewhat on the concentration. In this connection Ostwald[6] stated that the order of the cations of the Hofmeister series varied with the concentration as well as with the nature of the colloid and gave data which clearly showed this. The results in Table III indicate that each neutral sulfate is less effective than its corresponding chloride in the dehydration of Wyoming bentonite but the difference is so small as to be within the probable limit of error for the tests. Table III also shows a slight difference in the effects of neutral cations on the swelling of bentonite. Again the differences are so small as to preclude a sure statement as to the specificity of the ions, but the order in the case of the chlorides and sulfates, so far as it was determined, was the same. The series in the order of their greatest dehydrating effect for the normal and 3 normal solutions is, for the chlorides: K, NH_4, Na, Ca, Sr, Ba, Mg; and for the sulfates: K, NH_4, Na, and Mg.

Conclusions

From a consideration of its behavior, the gel of Wyoming bentonite appears to be an inorganic, hydrophilic colloid.

Material whose apparent expansion in water is evidently due to breaking down, as exemplified by samples from Texas and New Mexico, should cause trouble in wet drilling only through caving of the well walls, since the increase in volume is small and the resulting product is not pasty, but certain bentonites swell markedly in water and are known to cause the difficulties previously enumerated. The tests described herein lead to the conclusions that lubricating oil, kerosene, or gasoline could be used to replace water in wet drilling through bentonites to prevent swelling and breaking down. However, water would have to be excluded to prevent the formation of emulsions with their attendant problems. Cheap salts could be used to form dilute solutions that would cut down the swelling effect of bentonites in water considerably, but they would probably not prevent caving. The addition of a greater amount of these salts would apparently prevent practically all detrimental action of the solutions on bentonite. For some bentonites sodium chloride evidently gives satisfactory results; other bentonites, however, become soft in a saturated solution of this salt, indicating the possibility of breaking down and caving of the walls of wells being drilled through them. It seems possible that those bentonites which become soft in saturated sodium chloride solution may remain firm in a solution of some other common salt, so that drilling difficulties caused by bentonite may be overcome in all cases.

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[4] *Loc. cit.*

[5] "Colloid Symposium Monograph," Vol. II, p. 206 (1925).

[6] Fischer, Handbook of Colloid Chemistry, p. 168 (1915).

Micro Determination of Carbonate Carbon[1]

By Geo. Kemmerer and L. T. Hallett

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THE determination of carbon in the residues obtained by evaporating lake waters by the micro combustion method[2] requires an equally accurate method for the determination of the carbonate carbon present unless the carbonate is first decomposed by acid. The English Commission[3] used sulfurous acid, assuming that the excess would be volatilized and no sulfuric acid formed. Hydrochloric acid added to the water makes the residues too hygroscopic to weigh and no satisfactory method has been devised for treating the weighed samples of the residues with acid. To avoid the use of acid the micro combustions were made at 900–950° C. in order to decompose all carbonates. The carbonate carbon was then determined in a 5- to 15-mg. sample of the residue and subtracted from the total carbon determined by combustion.

Apparatus

The apparatus (Figure 1) is constructed of Pyrex glass. Wherever rubber connections cannot be avoided they are saturated with vaseline to prevent the absorption or liberation of carbon dioxide.[4] A rubber stopper is used in the 50-cc. extraction flask *A*, so that the flasks can be interchanged. The condenser, *M*, is approximately 20 cm. long with the central tube, *B*, beveled on the lower end so that it will not be closed by drops of condensed water. The trap, *P*, containing sulfuric acid, is sealed between the condenser and drying tube, *R*, containing the solid drying agents to absorb most of the water before it enters *R*. This trap also

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[1] Received June 13, 1927.

[2] Kemmerer and Hallett, THIS JOURNAL, **19**, 173 (1927).

[3] "Best Means of Preventing the Pollution of Rivers," Reports of Commissioners 22, House of Commons, 1874, Vol. 33.

[4] Pregl, "Quantitative Organic Micro-Analysis," p. 46, translated by Fyleman.

indicates the flow of gas through the apparatus. It can be readily emptied by means of the stopcock at the bottom and refilled through the same by applying suction to the apparatus. The drying tube, *R*, 26 cm. long, is made of a 1.7-cm. ground-glass joint, which is sealed with Kronig glass cement.[5] With Pyrex glass there is no danger of cracking while sealing.

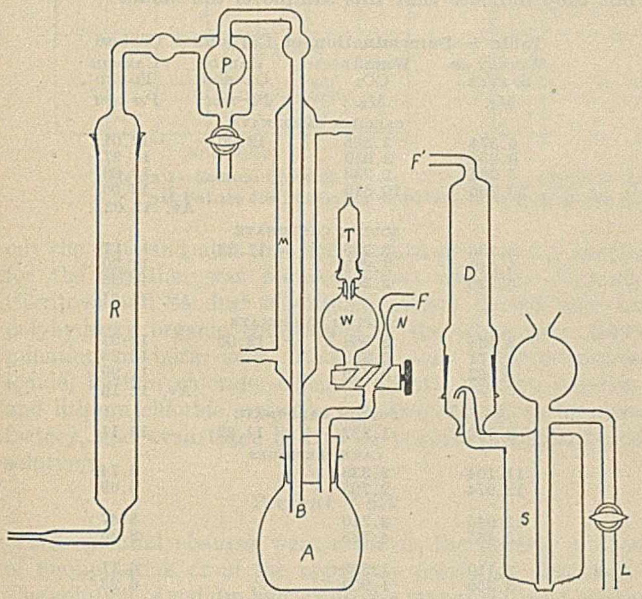

Figure 1—Apparatus for Micro Determinations of Carbonate Carbon

The drying tube is filled with magnesium perchlorate trihydrate (Dehydrite), ground so that about half of it will pass through a 20-mesh sieve. This is placed in 1-cm. layers, first coarse then fine, together with a layer of anhydrous copper sulfate about 3 cm. from the bottom.

The acid bulb, *W*, is attached to the flask *A* through a three-way stopcock and supplied with an Ascarite-filled guard tube, *T*, to prevent absorption of carbon dioxide from the air. The air drawn through the apparatus to remove the carbon dioxide is first drawn through a sulfuric acid trap, *S*, which can readily be emptied by disconnecting at *FF'* and blowing the sulfuric acid out through *L*. The trap is then refilled with acid through the funnel. The air then passes through the tube *D*, which is filled with Ascarite to absorb any carbon dioxide present. The constriction, *N*, retards the diffusion of the carbon dioxide liberated in *A* back into this tube. The whole apparatus is easily attached to a single ringstand.

Absorption Tube—The micro absorption tube for carbon dioxide is similar to the one described in the work on micro combustion,[2] except that the shape of the mercury pockets has been changed slightly, making the tube a little easier to manipulate and more easily constructed. The size of the capillaries and of the mercury pockets is very important and should be as nearly as possible as described (Figure 2).

The tube is made from a $^1/_4$-inch (6-mm.) Pyrex ground-glass joint, *E*. The main body of the joint is extended into a tube 7 cm. long and 1.3 cm. in diameter with thin walls to keep the weight as low as possible. The mercury traps at each end of the tube are identical. The internal diameter at *A* and *B* is 0.2 mm. The bulb *C* has an internal diameter of 3 to 4 mm. As an added precaution 2.5- to 3-mm. bulbs are blown between points *B* and *D* to catch any mercury which might be carried through. The straight part of the tube *D* has an internal diameter of 1 mm. and for a distance of 1.5 cm. an external diameter of 3 mm. which fits the specially treated micro tubing[6] used to connect it with the drying tube, *R*, and the guard tube. In Figure 2 the mercury is shown sealing the capillaries. When the tube is rotated 180 degrees and shaken slightly, the mercury falls into the pocket, *C*, and the tube is open. The ground-glass joint is sealed with Kronig glass cement.

The absorption tube is filled with a layer of cotton, 5 cm. of Ascarite which passes through a 10-mesh sieve, a small layer of cotton, and finally 2 cm. of pulverized Dehydrite, and the end protected with cotton.

Procedure

When the apparatus is freshly filled, carbon dioxide is passed through it and allowed to stand for 2 hours, or better, overnight. The carbon dioxide is then removed by passing air through the apparatus. This operation is repeated whenever the sulfuric acid is replaced in the trap, *P*. Ten- to 15-mg. samples of lake-water residues obtained by evaporating this water at 80° C. are placed on small cover glasses made by cutting the bottoms from test tubes, weighed on a micro balance, and transferred with the cover glass to the flask, *A*. The flask is then attached to the apparatus and air drawn through for 10 minutes to remove any carbon dioxide present in the flask or apparatus. Approximately 2 *N* hydrochloric acid which has been boiled to remove carbon dioxide is placed in the bulb *N*. The absorption tube, which has been stored under a bell jar after careful wiping, is attached to the apparatus while it is being swept out with air. This fills the tube with dry air similar to that which will fill it at the end of the determination.

As the apparatus is under a slight vacuum it is necessary, before removing the absorption tube, to bring the tubes to atmospheric pressure by removing the suction line from the guard tube or by opening a three-way stopcock placed in the suction line beyond the guard tube. One minute should elapse before removing the tube. The tube is then removed by touching only the end of the capillaries with the thumb and forefinger and sealed by rotating it 180 degrees and shaking gently. It is then placed on the micro balance, allowed to stand 15 to 20 minutes, and weighed. The tube is removed from the balance, rotating 180 degrees, shaken gently, and examined carefully to make sure that all the mercury has dropped into the pockets. It is then connected to the apparatus and the guard tube containing Dehydrite attached.

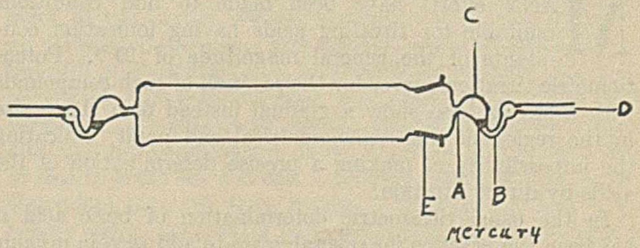

Figure 2—Micro Absorption Tube

Air is aspirated through the apparatus at the rate of 12 to 14 cc. per minute, and 5 cc. of hydrochloric acid are allowed to drop slowly into *A*. When the reaction is complete 5 minutes are allowed for the air current to sweep out most of the carbon dioxide. The flask *A* is then heated with a micro burner and the solution boiled 2 to 3 minutes. The air current is allowed to continue for 20 minutes more. After relieving the suction for 1 minute the tube is removed exactly as before, allowed to rest on the balance for 15 to 20 minutes, and weighed. While the tube is coming to constant weight on the balance, a second sample, which has been weighed and placed in a clean flask, is attached to the apparatus,

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[5] Pregl, *op. cit.*, p. 37.

[6] *Op. cit.*, p. 43.

which is then swept out with air as before while the tube is being weighed. The second determination is carried out exactly as the first.

Drying Agent

Since calcium chloride was not satisfactory as a drying agent in micro combustions,[2] it was not used here. Phosphorus pentoxide is a better dehydrating agent than Dehydrite and gives very satisfactory results if it is placed in the drying tube mixed with glass wool and in the end of the absorption tube. It takes up water so rapidly that great care must be exercised in using a guard tube of phosphorus pentoxide and in handling the absorption tube while it is open to the air. Where the amount of carbon dioxide weighed is less than 2 mg. it has been found advisable to use phosphorus pentoxide as the drying agent, but for practical work Dehydrite gives very satisfactory results. The one objection to Dehydrite is lack of any indication of its failing to absorb all the moisture, whereas with phosphorus pentoxide this point is more easily determined. The charge of Dehydrite in the absorption tube is sufficient to absorb the moisture during the life of one-half the Ascarite present, which will average around twenty determinations and is indicated by the Ascarite changing to a grayish white.

Results

The apparatus has been developed first for its accuracy and second for carrying out a large number of determinations. One of us, using this apparatus at the same time that he was running micro combustions, averaged eight determinations for each day of 9 hours. Around four hundred of these determinations have been made. The results given in Table I are typical of the whole series. On lake residues from soft-water lakes where there is a small amount of carbonate present the average error on checks is less than 0.1 per cent. With samples of Iceland spar a smaller sample can be used and the checks are better. One set of results is given where 2-mg. samples of calcium carbonate were used, but they indicate that this sample is too small.

Table I—Determination of Carbonate Carbon

Weight of Sample Mg.	Weight CO_2 Mg.	Calcd. Carbon Per cent	Carbon Found Per cent
	CALCIUM CARBONATE		
6.374	2.806	12.00	12.01
6.950	3.050		11.97
5.284	2.339		12.08
23.786	10.519		12.06
			Av. 12.03
	SODIUM CARBONATE		
8.100	3.345	11.32	11.27
5.540	2.293		11.29
5.290	2.202		11.36
			Av. 11.31
	CALCIUM CARBONATE		
2.138	0.958	12.00	12.22
1.971	0.886		12.26
1.652	0.726		11.99
			Av. 12.16
	SODIUM CARBONATE		
2.763	1.227	11.32	12.11
	LAKE RESIDUES		
11.104	2.338		5.74
12.974	2.705		5.69
11.945	3.710		8.47
15.465	4.735		8.35
7.110	1.592		6.11
8.359	1.909		6.23
11.788	1.965		4.55
16.862	2.820		4.56
12.190	2.294		5.13
14.600	2.794		5.22

Potentiometric Titration of Boric Acid in the Presence of Certain Inorganic Salts[1]

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Many efforts have been made to find conditions suitable for titrating acids having ionization constants of the general magnitude of 10^{-9}. Potentiometric titration curves for the reaction of such compounds with a strong base show a gradual instead of a sharp rise in the region of the stoichiometrical end point, indicating the impossibility of making a precise determination of the acids by direct titration.

In the usual titrametric determination of boric acid it has been the practice for several years to add certain organic compounds, such as glycerol or mannitol, to the solution to be titrated. Since satisfactory end points are obtained under these conditions, one would conclude that some marked change has occurred in the potentiometric titration curve for the acid. That such a conclusion is warranted has been shown by determinations of curves, first for the acid alone, and then for the acid in the presence of various polyhydroxy organic compounds.[2] These curves indicate a decided increase in hydrogen-ion concentration in a solution of boric acid following the addition of certain organic compounds to it. In this case it is generally assumed that the observed effect is due to the formation of an acidic complex more highly ionized than boric acid itself.

In addition to this phenomenon, now definitely recognized, one encounters the well-known action of certain neutral salts in increasing the hydrogen-ion concentration of acids. With this effect in mind, the object of the present paper was to study, by means of a determination of the potentiometric titration curves of boric acid alone, and of the acid in the presence of certain neutral salts, the effect of different salts and of different concentrations of the same salt on the course of neutralization.

Previous Work

Although the effect of neutral salts on the rates of catalyzed reactions, on solubilities, and on the apparent concentration of various ions has been the subject of many investigations since the time of the early work of Arrhenius,[3] the effect on the hydrogen-ion concentration of solutions of boric acid has received only minor attention. Prideaux noticed[4] that a dilute solution of boric acid saturated with sodium chloride required more sodium hydroxide than with-

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[1] Received July 18, 1927. Presented before the Division of Industrial and Engineering Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Van Liempt, *Rec. trav. chim.*, **39**, 358 (1920); *Z. anorg. Chem.*, **111**, 151 (1920); Mellon and Morris, This Journal, **16**, 123 (1924).

[3] *Z. physik. Chem.*, **1**, 110 (1887); **4**, 226 (1889); **31**, 197 (1899).

[4] *Z. anorg. Chem.*, **83**, 362 (1914).

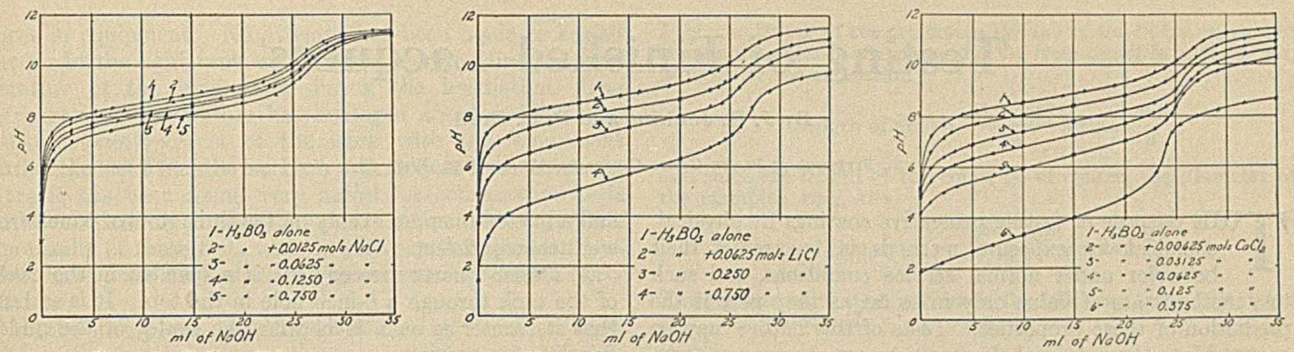

Figure 1—Sodium Chloride

Figure 2—Lithium Chloride

Figure 3—Calcium Chloride

pH Values for Titration of 50 ml. of 0.05 *M* Boric Acid by Itself and in Presence of Different Amounts of Salts

out the salt, and also that the amount of mannitol needed for the titration was reduced about one-half. Recently Cikritova and Sandra[5] substituted certain neutral salts for polyhydroxy organic compounds in the titrametric determination of boric acid. Although they tried potassium iodide, barium chloride, calcium nitrate, calcium chloride, and lithium chloride, only the last two seemed to be satisfactory, and even these had to be present in concentrated solutions.

Present Work

No essential changes were made in the general method of manipulation or in the apparatus previously described.[2] The solution of sodium hydroxide was prepared free of carbon dioxide. That for boric acid was made from recrystallized material and standardized as before. The salts were all purified by three recrystallizations and dried (except sodium chloride, which was precipitated from a saturated solution by means of hydrogen chloride gas). Aqueous solutions of these salts were neutral to bromthymol blue except in the case of calcium chloride, which was slightly alkaline, due presumably to overdrying.

In the determination of the potentiometric curves 50 ml. of 0.05 *M* acid were first titrated with 0.1 *M* base. Then like portions of the acid were titrated after dissolving weighed amounts of the various salts. For convenience of comparison, the quantities of salts were calculated, in terms of mols, as simple multiples of the amount of boric acid taken. The largest quantity of salt used in each case was approximately sufficient to saturate the solution under the given conditions.

The data for the titrations, shown in Figures 1 to 3, have been plotted in the conventional form, coördinating pH values and volume of titrating solution. Each curve represents an average of two or more sets of determinations.

Discussion

In the course of the collection of the data presented here the following salts were tried: lithium, sodium, potassium, and calcium chlorides, sodium and potassium sulfates, and sodium and potassium nitrates. A consideration of the results obtained with these different combinations reveals some interesting variations.

With sodium and potassium nitrates a more or less steady increase of potential was encountered, rendering the results quite unsatisfactory. It was assumed that reduction was occurring at the cathode,[6] and these salts were discarded. With the use of sodium sulfate, potassium sulfate, and potassium chloride the results obtained agreed so closely with those for boric acid alone that the curves have not been included. Considering the sources of error inherent in the method used, no conclusions are offered regarding the small displacement observed in the curves.

An inspection of Figures 1 to 3, showing the effect of sodium, lithium, and calcium chlorides, respectively, indicates that the capacity of these individual salts to increase the pH value of a solution of boric acid increases in the order of the salts named. The drop in the curve when using sodium chloride is not large, but there is a consistent change as the concentration of the salt is increased. The use of 0.375 mol of calcium chloride, on the other hand, produces a very marked drop in the curve.

Ultimately one is interested in ascertaining the mechanism producing the change in the curves shown, but thus far no one seems to have proposed a generally acceptable theory for the action of neutral salts in such systems. Although the present data hardly warrants any conclusions in this direction, it may be noted that lithium and calcium chlorides produce the most marked effect, a fact which may have some connection with their tendency to form hydrates.[5] A further point of interest arises in connection with solubility relationships. The data available [7] for the solubility of boric acid in solutions of lithium, sodium, and potassium chlorides show a qualitative agreement between the effect of the salts on the solubility of the acid and their effect on the pH value of solutions of the acid.

Potentiometric titration curves furnish valuable information regarding the proper indicator to use and the approximate degree of precision attainable for a given titration. Of the three salts mentioned as producing distinct displacement of the curves, sodium chloride would probably be of no value in a titration. Lithium chloride is somewhat better but still of doubtful value, as there is no marked rise in the curves at the stoichiometric end point. With the more concentrated solutions of calcium chloride the rise is better, although not steep in any case. Curve 6, Figure 3, is best in this respect; but the rise, curiously, does not occur where equivalent amounts have reacted. In order to stop at the proper place, apparently one should use rather the amount of salt indicated for curve 5—that is, a ratio of calcium chloride to boric acid of 50 to 1. This brings the rise of the curve on the border of the pH range of phenolphthalein. Even then, judging from the shape of the curve, one would not predict a high degree of precision. As a check on this prediction, several ordinary titrations were made with the higher concentrations of lithium or calcium chloride present. In eash case the change of color of phenolphthalein was too gradual to be called a good end point. In view of the relatively good results obtainable with the use of certain polyhydroxy organic compounds, the proposal of Cikritova and Sandra to use the salts mentioned seems of questionable value.

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[5] *Chem. Listy*, **19**, 179 (1925).

[6] Loomis and Acree, *Am. Chem. J.*, **46**, 621 (1911).

[7] Seidell, "Solubilities of Inorganic and Organic Compounds," p. 154 (1919).

Testing of Finished Lacquers[1]

By J. D. Jenkins and P. R. Croll

Pittsburgh Plate Glass Company, Milwaukee, Wis.

THE purpose of testing protective coatings by physical, chemical, or exposure methods is to predict their behavior under normal service conditions, and such test methods are of value only in so far as they permit the prediction of these properties. Tests of this nature may be grouped into three general classes: (*a*) normal exposure tests, (*b*) accelerated exposure tests, and (*c*) tests of physical and chemical properties of the film. This paper will be limited to the last two of these three groups and will include a description of the equipment and cycle in use at the Milwaukee Laboratories of the Pittsburgh Plate Glass Company for accelerated exposure tests and a discussion of three physical tests on finished lacquer films.

Accelerated Exposure Tests

Equipment—The accelerated exposure equipment used at the Milwaukee Laboratories comprises a refrigeration room and a light and moisture tank (Figure 1). The refrigeration room proper is 9 by 12 feet and 8 feet high. It is insulated by a 2-inch layer of cork and provided with a double window and a refrigerator door. Within this room is a tank 5 feet high and 6 feet in diameter, supplied by an individual air duct from the refrigeration equipment. The light and water tank is also 5 feet high by 6 feet in diameter. Both tanks are provided with hexagonal racks rotated by motors operating through speed reducers and bevel gears and so arranged as to rotate once every 10 seconds.

The panels are exposed in panel holders (Figure 2), which hold three 6 by 12-inch panels, bolted with brass bolts, one above another and spaced out from the holders by strips of beading $^1/_8$ inch square at the top and bottom of each panel. This spacing provides drainage and air circulation behind the panels. The holders are hung vertically from the top bar of the hexagonal rack by means of two small hooks on the back of the holder. The tanks are fitted with covers and the light tank is equipped with three spray nozzles set 1 foot apart on a vertical pipe and adjusted to spray evenly on the three rows of panels from a distance of 2 feet.

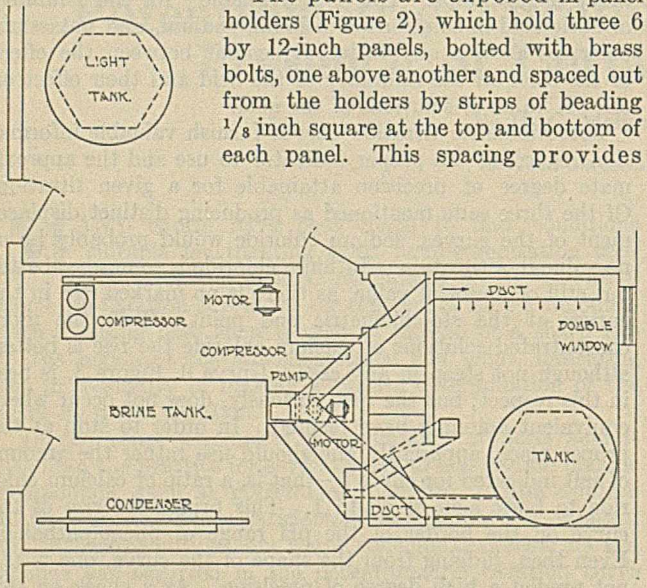

Figure 1—Plan of Weather Room

A 30-inch quartz mercury arc is suspended in the center of the tank through a 6-inch hole in the top. It is so hung that its center is on a level with the center of the middle panel.

The distribution of light upon the fifteen panels on each side of the hexagonal rack is shown in Figure 3. It may be assumed that over a relatively large number of changes, from the water-light tank to the refrigerator tank and back, the law of chance will cause any one panel holder to occupy each of the five possible positions an equal number of times; consequently, the variation of intensity between the middle position for the panel holders and the outside positions will be offset. The top and bottom panels, however, will always get less light than the corresponding center panel, about 90 per cent for the top and bottom as compared with 100 per cent for the center, and this can only be eliminated by changing the panels around. These values are all calculated figures using the formula:

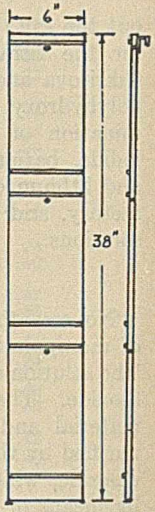

Figure 2—Panel Holder

$$\text{Intensity} = \sin\theta \frac{L-A}{r\sqrt{r^2+(A-r)^2}} + \frac{A}{r\sqrt{r^2+A^2}}$$

where L = length of quartz burner
A = distance to center of panel as measured vertically downward from level of top of light
r = distance to center of panel as measured horizontally from a line passing vertically through center of light
θ = horizontal angle between surface of panel and a perpendicular to the line passing vertically through center of the lamp

Method of Operation—The cycle used at present is as follows:

Monday:				
	11:30 A.M.	to	2:00 P.M.	Refrigeration
	2:00 P.M.	to	5:00 P.M.	Water, cold
	5:00 P.M.			
Tuesday:				
		to	8:00 A.M.	Light
	8:00 A.M.	to	11:30 A.M.	Water
	11:30 A.M.	to	2:00 P.M.	Refrigeration
	2:00 P.M.	to	5:00 P.M.	Light and water
	5:00 P.M.			
Wednesday:				
		to	11:30 A.M.	Light
	11:30 A.M.	to	2:00 P.M.	Refrigeration
	2:00 P.M.	to	5:00 P.M.	Light and water
	5:00 P.M.			
Thursday:				
		to	11:30 A.M.	Water
	11:30 A.M.	to	2:00 P.M.	Refrigeration
	2:00 P.M.	to	5:00 P.M.	Light and water
	5:00 P.M.			
Friday:				
		to	11:30 A.M.	Light
	11:30 A.M.	to	2:00 P.M.	Refrigeration
	2:00 P.M.	to	5:00 P.M.	Water
	5:00 P.M.			
Saturday:				
		to	10:00 A.M.	Light
	10:00 A.M.	to	12:00	Refrigeration
	12:00			
Monday:				
		to	11:30 A.M.	Light

It is very similar to the one used by H. A. Nelson, of the New Jersey Zinc Company, with some changes due to differ-

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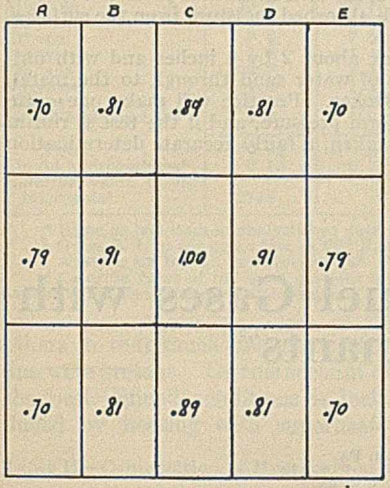
[1] Presented as part of the Symposium on Lacquers, Surfacers, and Thinners before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

ences in equipment. No attempt has been made to enrich the air in the light tank with oxygen, nor to raise the temperature of the light tank during the irradiation. The refrigeration temperature has averaged about −5° F.

Conclusions—Most of the work with this equipment during the last 9 months has been with lacquer-base materials. Here it has been found very useful for comparative tests between relatively similar materials. Attempts to correlate the results of these tests with outside exposure panels, however, have been less fruitful. The reasons for this are fairly obvious.

In the first place, the normal manner of failure of such finishes as automobile enamels and clear lacquers is by chalking or disintegration by light. However, the variation in the amount of sunlight and its content of the active short wave lengths, or ultraviolet light, is very marked between summer and winter. As a result, lacquers will be much longer lived during the winter than during the summer months on exterior exposure. In products which fail by cracking or checking the type of failure can usually be approximated, but the time ratio of accelerated to normal exposure varies somewhat.



A	B	C	D	E
.70	.81	.89	.81	.70
.79	.91	1.00	.91	.79
.70	.81	.89	.81	.70

Figure 3—Percentage Distribution of Light on Fifteen Panels on One Side of Hexagonal Rack

These results are, of course, preliminary and incomplete. Further data will be presented as they are obtained.

Tests on the Film

An apparatus for the control of the elongation at rupture and the tensile strength of lacquer films has been in daily use testing automobile enamels for nearly a year. This apparatus is an ordinary Mullen paper tester with a small, very simple attachment for indicating the elongation. The principle of this indicator will be plain from the diagram (Figure 4).

The lever arm, *L*, rests on the surface of the film, which is clamped over the rubber membrane. When the handwheel on the instrument is turned so as to force the plunger into the glycerol chamber and distend the rubber membrane, the film is bulged up and consequently stretched. This degree of bulging is a measure of the amount of stretch undergone by the film. The distention of the film moves the lever arm, *L*, up, causing the pointer, *P*, to travel across the scale *S*, which is calibrated directly in per cent elongation.

The calibration of the elongation scale is somewhat arbitrary. The elongation is calculated as the per cent increase in the length of the arc along a diameter of the circular opening in the clamping ring, as the film is bulged out in the form of a segment of a sphere. The elongation is expressed as

$$\text{Per cent elongation} = \frac{\text{length of arc} - \text{length of chord}}{\text{length of chord}}$$

The calculation of this scale giving the elongation as a function of the vertical movement of the top of the bulge is given below.

Let d = inside diameter of clamping ring
h = height of bulging of film

Then the length of the arc across the top of the bulge, measured along a diameter of the clamping ring from one side to the other, is given by the expression

$$\text{Length of arc} = \frac{d^2 + 4h^2}{2h} \text{ arc tan } \frac{2h}{d}$$

and since the length of the chord is, of course, the diameter of the clamping ring, the

$$\text{Per cent elongation} = \frac{d^2 + 4h^2}{2hd} \text{ arc tan } \frac{2h}{d} - 1$$

The per cent elongation is given in the following table, calculated as a function of h/d:

h/d	Per Cent Elongation	h/d	Per Cent Elongation
0.0	0.0	0.3	22.5
0.1	2.7	0.4	38.3
0.2	10.4	0.5	57.1

The nature of the stress applied to the film in this test is of interest. The edges of the circle are subject to a bending action and to elongation practically all in one dimension. The section of film near the center of the circle, however, is subject to elongation in two dimensions—i. e., to an increase in area. Consequently, the results of this test cannot, perhaps, be compared directly with the results obtained on the type of machine which stretches a strip of material in one direction only. Whether the results can be translated into per cent linear elongation or not, the test is a useful, duplicable, and reliable one for control work. The bursting pressure of the film is read directly on the gage provided with the instrument. It is desirable to get a gage for this work which indicates a maximum bursting pressure of about 25 pounds per square inch.

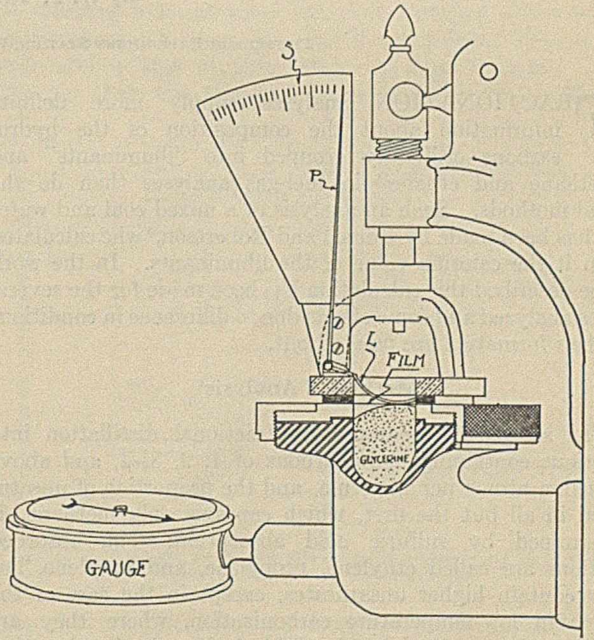


Figure 4—Paper Tester with Elongation Indicator

The preparation and drying of the films for test are important items. For factory control it has been found satisfactory to spray the films on amalgamated tin plates and force dry for 1¹/₂ hours at 50° C. Four or 6 ounces of the lacquer as ready for spraying are applied per square foot of surface in two or three coats, two fluid ounces per coat, drying just long enough between coats to lose the wet appearance. The 1¹/₂-hour forced drying has been found about equivalent to 24-hour drying at room temperature, and is long enough to attain conditions sufficiently constant for this type of work. A small constant temperature electric oven fitted with a rotating rack for the panels has proved very satisfactory for drying purposes as it insures uniform temperature and air circulation during drying.

The apparatus is not satisfactory for testing films with less than 1 per cent or more than 25 per cent elongation, but since most lacquers for automobiles usually fall within these limits this is not a serious disadvantage.

Contraction or Paper-Curling Test

Another test which has been found useful for control work to indicate the presence of the proper amount of plasticizer in a lacquer product is a paper-curling test. The lacquer product is sprayed on a standard 6 by 8-inch card (Velvo, 110 lbs. per ream, enameled paper has been found satisfactory) and dried under the conditions the product is to meet. Lack of plasticizer evidences itself by a very pronounced contraction of the lacquer on drying and a consequent strong curling of the paper. This test, if carefully made, is an excellent check upon the condition of the finished product.

Sanding of Lacquers and Surfacers

Tests of the ease of sanding of lacquers and surfacers are important under certain conditions. Two methods of such tests have been tried for surfacers and found about equally satisfactory. The first step in each is to spray a measured amount of the surfacer over primer or bare metal, dry under the conditions the surfacer is to meet, and sand as follows:

(*a*) Weigh the panel, sand a given number of strokes evenly distributed over the whole panel, wash off, dry, and weigh again. The panel should be given some time in a warm place to dry after sanding in order to remove absorbed moisture from the surfaces. Repeat and take an average.

(*b*) Use a sanding block about 2 by 4 inches and with uniform pressure and plenty of water sand through to the metal, counting the number of stokes. Practice will make one quite proficient at giving a uniform pressure, and if the test is run in triplicate and an average taken, a fairly accurate determination is obtainable.

Fractionation Analyses of Several Fuel Gases with Special Reference to Illuminants[1,2]

By W. P. Yant and F. E. Frey

Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

FRACTIONATION analyses supply more definite information about the composition of the hydrocarbons ordinarily grouped into "illuminants" and "methane and ethane" in fuel-gas analyses than do the usual methods. Such an analysis of a mixed coal and water gas has been made by Burrell and Robertson,[3] who calculated from it the calorific value of the illuminants. In the work to be described this calculation has been made for the several gases analyzed and some effects due to difference in conditions of their formation are pointed out.

Method of Analysis[4]

The sample is separated by fractional distillation into fractions containing hydrocarbons of 1, 2, 3, 4, and above 4 carbon atoms per molecule, and the proportion of unsaturated in all but the first, which contains only methane, is determined by sulfuric acid absorption. The absorbed portions are called ethylene, propylene, and butylene, but may contain higher unsaturates, except in the case of the gas from low-temperature carbonization, where they are known to be nearly absent.[5] Table I gives the fractionation analyses.

Origin of Gases Analyzed

Low-Temperature Carbonization—The gas produced by internal heating in the Karrick retort was formed by the carbonization of a non-coking coal (12.3 per cent oxygen and 42.9 per cent volatile matter) descending continuously in an insulated vertical chamber through which superheated steam passed from bottom to top. The carbonization by external heating in the same retort was conducted in a 3.5-foot (1.07-meter) section of the chamber, 7 inches (18 cm.) inside diameter. The inside wall was held at 500° C. and at 850° C. throughout the two carbonizations.

The gas produced in the McIntire retort came from a coking coal. The coal was agitated in an externally heated chamber and distilled in an atmosphere of its own gas. The conditions of carbonization in both retorts have been given in detail elsewhere.[6]

High-Temperature Carbonization—The gas was produced from Klondike coal (7.1 per cent oxygen and 32.1 per cent volatile matter) and similar coals by the older type Koppers by-product oven in which a wall temperature of about 1120° C. was maintained. The oven was 16 to 18 inches (40 to 45 cm.) wide and the coking period 18 hours. This is the only one of the gases analyzed which was scrubbed to remove oils.

Water-Gas Process—The "blue gas" was obtained from anthracite and from coke, and carbureted in each case. For carbureting each blue gas, 3.2 gallons of oil per 1000 cubic feet of gas were used. The period of oil introduction was 0.75 to 1.25 minutes. The gas left the carburetor at 760–820° C.

Mixed Coal and Water Gas—The analysis of Pittsburgh manufactured gas by Burrell and Robertson[3] has been included.

Oil-Cracking Process—Crude petroleum was cracked for the purpose of obtaining a large yield of hydrocarbon gas of high calorific value. The oil was sprayed with steam into the tubes heated to about 750° C. The cracking took place largely in the vapor phase.

Effect of Conditions on Composition of Gas

Table II shows the composition of the hydrocarbon group in several different types of gas selected from Table I. The gases from low-temperature carbonization differ from the

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[1] Presented before the Division of Gas and Fuel Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Published with the approval of the Director, U. S. Bureau of Mines.

[3] *Chem. Eng.*, **20**, 223 (1914).

[4] Frey and Yant, This Journal, **19**, 492 (1927).

[5] *Ibid.*, p. 488.

[6] This Journal, **19**, 21 (1927).

Table I—Fractionation Analyses
(Percentage by volume on air-free basis)

CONSTITUENT	LOW-TEMPERATURE CARBONIZATION				HIGH TEMPERATURE CARBONIZATION	WATER GAS				OIL-CRACKING PROCESS	MIXED COAL AND WATER GAS[c]
	KARRICK RETORT			MCINTIRE RETORT		FROM COKE		FROM ANTHRACITE			
	Internal heating by steam 600° C.	External heating			Koppers ovens (scrubbed to remove benzene)						
		500° C.	850° C.	External heating		Blue gas	Enriched gas	Blue gas	Enriched gas		
Carbon dioxide	18.6	15.7	8.6	8.8	2.2	3.0	0.9	3.9	3.3	(CO_2) 0.0	(CO_2) 2.63
Hydrogen sulfide											(O_2) 0.81
Nitrogen	1.05	0.0	0.9	1.5	1.0	9.5	6.8	1.6	4.2	0.0	4.23
Hydrogen	10.1	14.5	55.95	23.4	57.2	43.8	37.4	50.57	38.4	19.0	37.33
Carbon monoxide	11.5	8.6	14.9	4.7	5.8	43.2	35.0	42.9	31.0	0.8	13.25
Methane	40.3	43.75	15.0	46.4	29.2	0.5	8.1	1.0	12.7	27.1	31.13
Ethylene	1.9	1.30	1.00	1.60	2.50	0.0	6.7	0.03	6.9	33.5	6.05
Ethane	7.4	7.6	1.32	6.7	1.35	0.0	1.30	0.0	1.05	3.5	2.10
Propylene	1.8	1.4	0.58	1.30	0.29		1.50		0.87	8.7	0.60
Propane	2.7	3.2	0.46	2.0	0.11		0.25		0.08	0.3	0.43
Butylene	1.4	1.2	0.37	0.65	0.18		0.75		0.45	4.8	0.11
Butane	0.95	0.85	0.17	0.85	0.04		0.0		0.0	0.1	..
Liquid hydrocarbons	2.3	1.9	0.75	2.1	0.13		1.30		1.05	2.2	(C_6H_6) 1.33
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Liquid hydrocarbons[a]	0.12	0.10	0.04	0.11	0.006		0.055		0.044	0.097	
Calorific value of illuminants[b]	2748				1840[d]		2077		1972	1935	2141

[a] Same as last item in analysis but determined as cc. of liquid per liter of gas.
[b] Gross B. t. u. per cubic foot at 60° F. and 29.92 inches Hg.
[c] Analysis by Burrell and Robertson.[3] Not calculated air-free.
[d] Calorific value of the same gas plus 0.7 per cent benzene—2108. This gas was not available unscrubbed. The value of 0.7 was determined in an available but less representative sample.

others in that much undecomposed higher paraffins and olefins were present. On this account only the one formed under the best defined conditions is included—namely, that produced by heating with superheated steam.

Table II—Composition of Hydrocarbon Group in Different Types of Gas
(Figures in per cent)

CONSTITUENT	LOW-TEMPERATURE CARBONIZATION	OIL CRACKING	CARBURETED WATER GAS		HIGH-TEMPERATURE CARBONIZATION
	Karrick retort[a]		From coke	From anthracite	Koppers ovens
	I	II	III	IV	V
A					
Ethylene	10.3	63.4	56.6	66.0	48.8
Ethane	40.3	6.5	11.1	10.0	26.3
Propylene	9.8	16.4	12.8	8.4	5.7
Propane	14.7	0.5	2.2	0.8	2.1
Butylene	7.6	9.0	6.2	4.3	3.5
Butane	5.2	0.2	0.0	0.0	0.8
Liquid hydrocarbons (as vapor)	12.1	4.0	11.1	10.5	12.8
Total	100.0	100.0	100.0	100.0	100.0
B					
Ethylene + ethane	50.6	69.9	67.7	76.0	75.1
Propylene + propane	24.5	16.9	15.0	9.2	7.8
Butylene + butane	12.8	9.2	6.2	4.3	4.3
C					
$\frac{\text{Ethylene} \times 100}{\text{Ethylene} + \text{ethane}}$	20.4	90.5	83.6	86.8	65.0
$\frac{\text{Propylene} \times 100}{\text{Propylene} + \text{propane}}$	40.0	97.0	85.3	91.3	73.1
$\frac{\text{Butylene} \times 100}{\text{Butylene} + \text{butane}}$	59.3	98.0	100.0	100.0	81.5
Liquid hydrocarbons, per cent unsaturated	75.0[b]	100.0[c]	100.0[d]	100.0[d]	100.0
Hydrogen, per cent in gas	10.1	19.0	37.4	38.4	57.2

[a] Per cent in total hydrocarbons excluding methane.
[b] Separate determination; no aromatics detected.
[c] Roughly 25 per cent aromatic, 75 per cent olefinic; very little saturated.
[d] Assumed; largely benzene.

By comparison of these analyses several effects appearing with increasing thermal decomposition become noticeable. They have been arranged in order of increasing temperature attained in the formation of the gas, and presumably of increasing degradation of the hydrocarbons. The degradation of the larger molecules into smaller through fracture causes an increase in the concentration of the latter at the expense of the former.

Figure 1 shows the effect of increasing decomposition on the relative proportions of the different sizes of hydrocarbon molecules. Butane plus butylene decreases considerably as the cracking becomes more complete, propane plus propylene decreases in the same way but to a somewhat less degree, while ethane plus ethylene shows a large increase. This indicates that the stability of ethylene is much greater than that of the other hydrocarbons determined, except methane. The final formation of the very stable methane in increasing amounts with increasing degradation is shown by the analyses of the oil-cracking gas and water gases in Table I. The gases from coal carbonization cannot be included in the comparison because of the large amounts of methane formed in the later stages of carbonization.

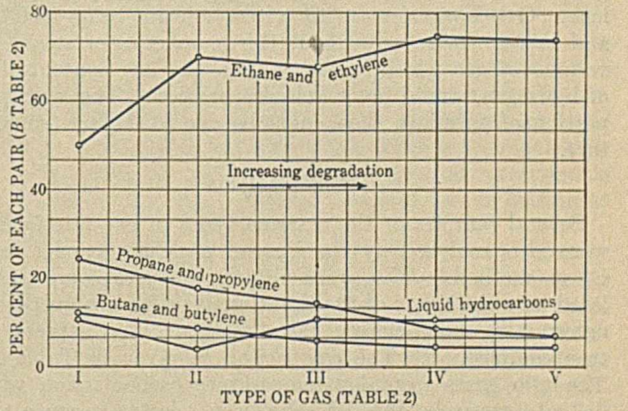

Figure 1—Change in Composition with Respect to Molecule Size with Increasing Degradation

The liquid hydrocarbons from gas I contained no aromatics,[7] from gas II roughly 25 per cent aromatic, while III, IV, and V were presumably chiefly aromatic.

As the quantity of liquid hydrocarbons carried by the gas is affected by the gas volume and extent of scrubbing by condensed tar, the determined quantities are not strictly comparable. However, in gases III, IV, and V the amounts of propylene and butylene present are small by comparison with them. This may be due in part to their conversion

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[7] Brown and Cooper, THIS JOURNAL, 19, 26 (1927).

Table III—Comparison of Fractionation Analysis with Usual Orsat Analysis
(Figures in per cent)

CONSTITUENT	LOW-TEMPERATURE CARBONIZATION				HIGH-TEMPERATURE CARBONIZATION[c]		CARBURETED WATER GAS			
	KARRICK RETORT									
	Steam at 500° C.		Steam at 850° C.		Koppers ovens		From coke		From anthracite	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
$CO_2 + H_2S$	22.3	22.3	11.5	11.5	2.4	2.4	0.9	0.9	3.3	3.3
N_2	1.2	0.0	0.6	0.0	0.9	0.5	6.8	6.9	4.2	3.6
O_2	0.2	0.0	0.2	0.4	0.0	0.0	0.0	0.0	0.0	0.0
H_2	3.3	3.3	43.1	43.0	56.4	56.5	37.4	37.2	38.4	38.6
CO	9.8	9.6	13.0	13.1	5.7	5.6	35.0	35.0	31.0	31.3
CH_4	23.5	25.6	21.4	23.8	29.3	29.6	7.9	7.9	12.6	12.7
C_2H_6	30.0	29.4	7.5	5.8	1.5	1.3	1.8	1.7	1.2	1.0
Illuminants	9.7	9.8	2.7	2.9	3.8	4.1	10.2	10.4	9.3	9.5
Total	100.0	100.0	100.0	100.5	100.0	100.0	100.0	100.0	100.0	100.0

A—Fractionation analysis calculated into terms of Orsat analysis.
B—Actual Orsat analysis of same sample.
[c] A different sample of unscrubbed gas from same ovens.

into aromatics. Zanetti and Leslie[8] obtained aromatics by thermal decomposition of a propane-butane mixture and an ethane-propane mixture. The yield was much the poorer in the second case.

The dissociation of a paraffin according to the reaction $RCH_2CH_3 \rightleftarrows RCH : CH_2 + H_2$ increases with temperature and decreases with increase in hydrogen concentration. The effect of variation in temperature and hydrogen concentration on the ratio of olefin to olefin plus paraffin is shown in Figure 2. The ratio is in every case greater for propylene than ethylene, and still greater for butylene. Gases II, III, IV, and V, all of which were exposed to temperatures above 750° C., show an increasing hydrogenation of each olefin with increasing concentration of hydrogen.

An equilibrium state with respect to this reaction is probably approached, with increasing dissociation, at a given temperature, in the order ethylene, propylene, butylene. Gas I was formed at a temperature below 600° C. and in the presence of about thirty volumes of steam per volume of gas which, together with the low concentration of hydrogen, would favor dehydrogenation. The large proportion of paraffins, then, must be due to the low temperature.

Orsat Analysis

Several samples of the extreme types of gas fractionated were also analyzed by the Bureau of Mines copper oxide Orsat method.[9] The fractionation analyses were calculated into the terms of the Orsat analysis for the purpose of determining how closely the Orsat analyses express the true composition. The comparison is given in Table III. The two gases from low-temperature carbonization which do not appear in Table I have been selected because they differ in content of illuminants and paraffins. They result from different degrees of devolatilization of the coal by superheated steam. Illuminants was taken as ethylene plus propylene plus butylene plus unsaturated fraction of liquid hydrocarbons. Methane and ethane was obtained from the contraction: CO_2 ratio calculated for methane plus ethane plus propane plus butane plus saturated fraction of liquid hydrocarbons ($C_{5.5}H_{13}$). The agreement between calculated and performed analyses is close for all the types of gas.

The Orsat value for illuminants is slightly greater (about 0.2 per cent) than the calculated value in every case, and this discrepancy is no greater for the gases rich in higher paraffins than the others. Solubility of higher paraffins, then, is not a serious source of error for such gases, when the gas is passed just six to eight times into the fuming sulfuric acid (30 per cent SO_3).[9] The Orsat value for methane is higher and for ethane lower than the calculated value. As a large variation in methane and ethane is caused by a small difference in the contraction-CO_2 ratio, a considerable variation does not indicate a faulty analysis. The slow-combustion method tends to give a contraction-CO_2 ratio slightly too high, possibly because of carbon or aldehyde deposition in the combustion tube or caustic spray in the train above the pipet. An error of this kind, of the magnitude found in these analyses, does not greatly affect a calculation of calorific value. The Orsat value for nitrogen is usually 1 per cent or so too low; hence, as it is determined by difference, the amount of some other constituents must be fictitiously large. The erroneously high contraction-CO_2 ratio mentioned raises the "methane plus ethane." This effect, as well as the temporary retention of combustible vapors in stopcock grease during the first part of the analytical procedure, may be responsible for the low nitrogen value.

Calorific Value of Illuminants

The gross calorific value of the illuminants (60° F. and 29.92 inches Hg) has been given in Table I for each gas.

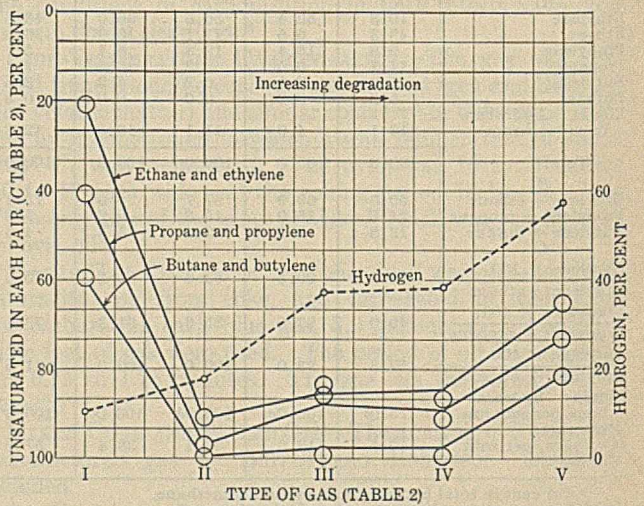

Figure 2—Effect of Hydrogen and Temperature on Proportion of Each Olefin

They were calculated from the composition of illuminants shown by the fractionation analysis. The calorific values in gross B. t. u. per cubic foot taken for the hydrocarbons are as follows: ethylene, 1583; propylene, 2340; butylene, 3089; benzene, 3741; pentylene, 3835; and hexylene, 4564.[9,10] The percentage of liquid hydrocarbons taken into

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[8] THIS JOURNAL, 8, 777 (1916).

[9] Burrell and Seibert, revised by Jones, *Bur. Mines, Bull.* 197 (1926).

[10] The value for hexylene was calculated from a molar heat given by Swietoslawski, *J. Am. Chem. Soc.*, 42, 1094 (1920).

the illuminants is the determined unsaturated portion of the fraction given in Table II. Its average formula is taken as $C_{5.5}H_{11}$ from the vapor-liquid volume ratio. The greatest source of error is in the determination of percentage of liquid hydrocarbons. In using these fractionation analyses as an aid in the calculation of calorific value from Orsat analyses, it would be better to substitute a percentage of liquid hydrocarbons determined more accurately than in these analyses on a larger volume of gas.

Determination of Volatility of Gasoline[1]

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The dew point is the best indication of the temperature of complete vaporization, under equilibrium conditions, of gasoline alone or mixed with air. This dew point may be determined easily, rapidly, and reliably by means of an optical effect shown by a new device called the "black-surface dew indicator."

The disadvantage of actually determining the dew points of the different air-fuel mixtures may be avoided by the use of a graph showing the relation between the dew point of the gasoline alone at 760 mm. pressure and the dew points of the different air-gasoline mixtures. This equilibrium end point or dew point of gasoline alone is especially easy to determine with the black-surface dew indicator, and its relation to the dew points of the air-gasoline mixtures is sufficiently definite for their derivation by means of a graph with practical accuracy. In this way, one simple determination of the dew point of gasoline alone suffices for the deduction of the temperatures of complete vaporization of all the practical air-gasoline mixtures.

SINCE the use of gasoline as a fuel in internal-combustion engines requires its preliminary vaporization to some extent, the measurement of its volatility has always been considered important. Until recently the only method for determining this volatility has been the Engler distillation or, as it is now called, the A. S. T. M. distillation.

It has long been recognized that this is an unsatisfactory method, for a number of reasons, particularly because fractionation is not the procedure of the vaporization that actually occurs in good practice in an automobile. Fractionation is the process of separation, whereas in the preparation in the automobile manifold of a gas mixture for combustion in the cylinders one seeks to integrate the vapors and have them so uniformly mixed that the gas mixture is one-phase. This is the procedure of equilibrium vaporization, which consists in such a coördination of thorough mixing with heating that at each stage throughout the process the liquid droplets are in substantial equilibrium with their entire environment until completely vaporized. This method of equilibrium vaporization not only offers complete or partial vaporization at the minimum temperature, but it is also the means whereby the exceedingly rapid vaporization required for automobile operation is attained. The velocity of vaporization is not a linear function of the temperature but is directly proportional to the velocity of mixing.

It is unnecessary here to insist further upon equilibrium vaporization, since the general trend in automotive practice is now towards it use. It is mentioned to show the need for a method of measurement of volatility which will correspond to equilibrium conditions instead of the present method of fractional distillation.

Wilson and Barnard[2] applied to gasoline Rosanoff's method of producing an equilibrium solution—that is, a solution in equilibrium with the vapors of completely vaporized gasoline. They determined the vapor pressure of this equilibrium solution of gasoline, thus obtaining the temperatures of complete vaporization at different partial pressures. However, these values were far from correct and they have abandoned this method. In subsequent work Wilson and others[3] have used the temperature at which the equilibrium solution is produced as indicative of the relative volatility of gasoline liquid itself. This method requires a large sample of gasoline, takes several hours to carry out, and precision is not readily obtained.

Stevenson and Stark[4] made a study of equilibrium vaporization and they developed their phase-change method for determining the temperature of complete vaporization of gasoline at 760 mm. partial pressure under equilibrium conditions. This equilibrium end point was called the Deppé end point and was proposed as a substitute for the Engler distillation. The method is precise and the point is one of perfect equilibrium. It is, however, difficult and requires too much time for rapid industrial use. Therefore the present investigation was carried out to discover a more practical way to determine this point.

The Deppé end point applied only to gasoline at 760 mm. partial pressure. The same phase-change method for determining equilibrium end points was applied with more labor and less precision to partial pressures less than atmospheric corresponding to the range of air-gasoline mixtures used in automobile operation. The present new and practical method of determining the equilibrium end point at 760 mm. partial pressure has been modified to apply to air-fuel mixtures.

Gruse[5] made air-gasoline mixtures and determined with reasonable accuracy the dew points by means of the familiar method of the internally cooled mirror. The authors, however, do not consider countercurrent evaporation as a proper means of securing equilibrium conditions.

Others[4,6] have determined the dew points of definite air-gasoline mixtures in closed flasks. However, in closed flasks the temperature is liable to be low because of the decrease in concentration of the gasoline vapors on account of absorption on the walls of the flask and on account of the condensation necessary at the time of measurement. (Table I)

All these methods refer to the determination of complete vaporization. Sligh[7] has devised a method for determining

[1] Received July 13, 1927. Presented before the Division of Petroleum Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] This Journal, 13, 906 (1921).

[3] *J. Soc. Automotive Eng.*, 12, 287 (1923).

[4] This Journal, 17, 679 (1925).

[5] *Ibid.*, 15, 796 (1923).

[6] Kennedy, *Bur. Standards, Sci. Paper* 500.

[7] *J. Soc. Automotive Eng.*, 19, 151 (1926).

partial volatility. It is not the purpose of this article to expound the reasons for the advantages of employing complete rather than partial vaporization in the manifold of an automobile. The writers do claim, however, that even when the automobile is designed to employ partial vaporization under equilibrium conditions, the determination of total volatility is a better indication of the value of a fuel for this automobile's operation than is the determination of partial volatility. This is so because a knowledge of the volatility of the residue of liquid is important since this residue is sometimes vaporized in the manifold, it is sometimes vaporized in the cylinder before combustion, and it should always be vaporized before the end of combustion.

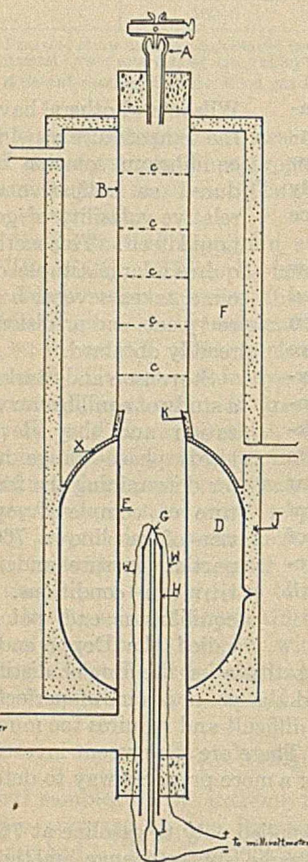

Figure 1—Apparatus for Determining Equilibrium End Point of Gasoline

Sligh[7] and Brown[8] employ the method of partial vaporization of gasoline under equilibrium conditions, with the subsequent separation of the vapor and the measurement of the volume of the liquid residue. Since the liquid gasoline is metered, the volumetric fraction of vaporization at a given temperature is at once calculated. This method does not readily permit the direct determination of the temperature corresponding to any given partial vaporization which may have been stipulated as the optimum degree of vaporization for automobile practice. This temperature is obtained by repeated trial, each time changing the temperature of the bath. Furthermore, this method is never precise because of the errors of such a large area of drainage combined with the measurement of small volumes in a graduate, and this inaccuracy increases with the extent of vaporization. It is not at all adapted to the direct measurement of the total volatility, since that point is obtained only by extrapolation of an unknown curve.

The apparatus and method of Sligh give a temperature of vaporization higher than the minimum temperature obtained under perfect equilibrium conditions. In fact, the writers have constructed a Sligh apparatus and have proved that fuel-air mixtures above the temperatures at which they show complete vaporization under perfect equilibrium conditions in their own apparatus still give a liquid residue according to Sligh's method of measurement in the Sligh apparatus. The temperatures corresponding to perfect equilibrium are the minimum temperatures at each stage of the vaporization. The method of Sligh gives temperatures which are too high; for example, a 15:1 air-fuel mixture of gasoline "E," which showed a dew point of 60.5° C. by the writers' method, was vaporized only to the extent of 98 per cent at 60.5° C. in the Sligh apparatus. The minimum temperature of complete vaporization is, by definition, the equilibrium temperature.

The new and practical methods for the determination of complete vaporization (total volatility), under perfect equilibrium conditions, of liquid gasoline and of gasoline in its admixtures with air, will now be described.

Equilibrium End Point of Gasoline

APPARATUS—The apparatus employed to determine easily, quickly, and accurately the equilibrium end point at 760 mm. partial pressure of complete gasoline vapor is shown in Figure 1. It consists of the following parts:

(1) A dropping funnel of about 50 cc. capacity. Only the tip, *A*, where it enters the vaporizer, is shown in the figure.

(2) The vaporizer, *B*, which is a tube of copper 1.2 cm. internal diameter and 20 cm. long, into which are cast five 40-mesh copper screens, *C*. The hot walls and the hot screens heat the gasoline and its vapor in stages, and at each stage the droplets are caught on the screens where they are directly heated while scrubbed with the gasoline vapors. The screens also homogenize the mixture. It was inferred that this would give practically perfect equilibrium vaporization, and tests indicate that this is true.

(3) A Dewar bulb, *D*, 6.5 cm. o. d., 1.9 cm. i. d., and 7.6 cm. long, fits tightly into the lower end of *B* by using a cork stopper. A part of the inner wall, *E*, near the top is frosted to indicate the presence of any unvaporized gasoline.

(4) The vaporizer and, to some extent, the upper part of the Dewar bulb are heated by means of the jacket, *F*, 6.5 cm. o. d. and 20 cm. long, which carries a stream of superheated steam or hot air. The heating jacket and the Dewar bulb are heavily lagged, *J*. The heating of the upper part of the Dewar bulb is accomplished by steel-wool packing, *X*, between the bulb and the heating jacket.

(5) The heater of the steam or air is shown in Figure 3, *S*. It is of the usual type and is heated by a Bunsen burner. Superheated steam is preferred to hot air. The temperature of this entering stream is indicated on the thermometer, *T* (Figure 3).

(6) The bottom of the Dewar bulb consists of a T-tube, the branch, 1.3 cm. i. d., going to the condenser as indicated and the straight end serving for the insertion of the black-surface dew indicator.

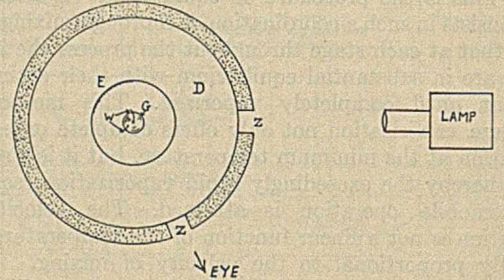

Figure 2—Slits in Lagging of Dewar Bulb

(7) This black-surface dew indicator is a platinum blowpipe tip, *G*, carrying an iron and a constantan wire, *W*, of about 25 B. & S. gage, soldered into the apex and about 2 mm. from the apex, respectively. These wires go back to a millivoltmeter. The platinum tip is sealed to the top of a soft-glass tube, *H*, 0.6 cm. i. d., by fusion with lead glass. The tip is cooled internally by means of a regulated flow of compressed air through the glass tube, *I*. The platinum tip is covered with a fine, thin, adherent plating of platinum black. It is conveniently cleaned by dipping in benzene. This tip shows at once the presence of any condensed liquid by an obvious optical phenomenon. There are two slits, *Z*, Figure 2, about 0.6 cm. wide by 5 cm. high in the lagging of the Dewar bulb; through one of these slits comes the illumination such as is used for microscopes and through the other slit the observer notices the optical change. When the tip is very wet it shines very brightly and when less wet it glistens. Even the slightest condensation is immediately obvious by a darkening or smoothness of appearance. The optical effect is not only a surface phenomenon but the condensed liquid also per-

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[8] Group Session, Motor Fuels, Society of Automotive Engineers, December 8, 1926.

mits the light to reach the bright metal underneath and to be reflected back to the observer's eye.

PROCEDURE—The procedure has already been suggested in the description of the apparatus. The illuminator is turned on, the superheater started, and the air or steam passed through it. The thermometer in this stream should register about 230° to 260° C.

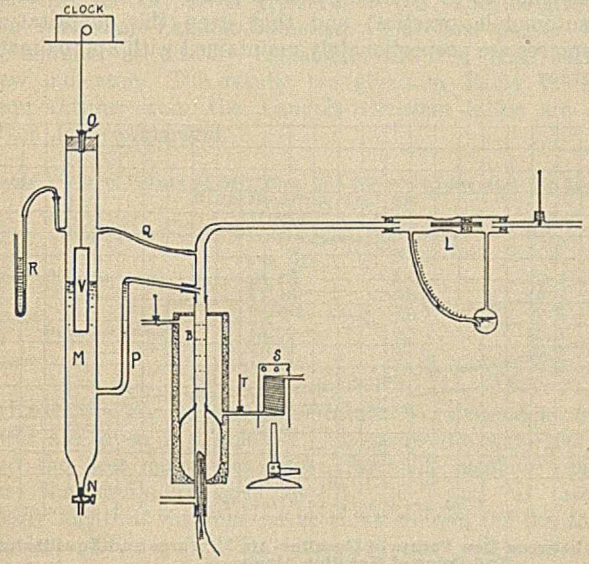

Figure 3—Apparatus for Determination of Dew Points of Air-Gasoline Mixtures

About 30 cc. of the sample of gasoline are put into the dropping funnel and the stopcock is turned on to give a flow such that the drops are not quite separate.

The frosted part of the tube wall of the Dewar bulb and the appearance of the platinum-black tip show whether there is complete vaporization. If this wall is wet, the temperature of the superheated steam must be raised.

The platinum tip is cooled by the compressed air. At the first appearance of condensation the temperature of the tip is noted. It should be 8° to 16° C. lower than the temperature of the uncooled tip. After practice this range of superheat is at once realized without further adjustment.

Having thus obtained complete vaporization of enough gasoline to give an atmosphere of exclusively gasoline vapor maintained at sufficient superheat to insure against any unvaporized residue and against any condensation except on the internally cooled tip, and having determined the approximate temperature of condensation, one now proceeds to get the precise temperature. This is done by cooling the tip rapidly by a large stream of compressed air to the approximate temperature and then cooling slowly until moisture just appears on the tip between the two wires. This is the temperature of condensation. It denotes the temperature of complete vaporization more accurately than a direct determination of the attainment of complete vaporization, even as the accurate determination of a boiling point is always made by determining the condensation point. At the initial condensation point there is complete vaporization, a condition of perfect equilibrium with a uniform vapor phase. The point as measured must be corrected to 760 mm. at the rate of +0.04° C. per mm. below 760 mm.

When the equilibrium end point is thus determined for any sample of gasoline, the gasoline remaining in the dropping funnel is removed, 10 cc. of the new sample are added and allowed to run out displacing the vapors of the previous sample, then 30 cc. more of the new sample are added. The feed is not turned off during this change of sample, and after about 3 minutes everything is ready for cooling the tip to get the new condensation temperature. Thus, when ten samples are to be tested each should not take longer than ten minutes. The error should not exceed 0.5° C.

VERIFICATION—The direct heating of the liquid on the walls and particularly on the heated screens while maintaining the liquid in intimate contact with its vapors, the scrubbing effect of the moving vapors, and the mixing effect of the spaced screens are conditions which tend to produce equilibrium vaporization so that one phase of vapor is formed at the minimum temperature.

However, while approximating a volatilization under equilibrium condition, it is recognized that the attainment of perfect equilibrium by rapid vaporization is impossible at the precise end-point temperature. Therefore, the vaporized gasoline is somewhat superheated and is given a little time to establish homogeneity by mutual diffusion and then this monophasal vapor is cooled down to a point where a slight amount of condensation occurs. Even this slight condensation does not at all affect the concentration of the gasoline at the moment the temperature is measured, because the gasoline vapor from which the condensation has occured is no longer present but has been succeeded by complete gasoline vapor. Therefore, the point of initial condensation in a stream of vapor gives the true temperature, which is slightly higher than that obtained in the closed-flask methods.

Further evidence that the vaporization has proceeded under approximately equilibrium conditions is shown by the remarkable velocity with which the gasoline is evaporated. It is only by the maintenance of approximate equi-

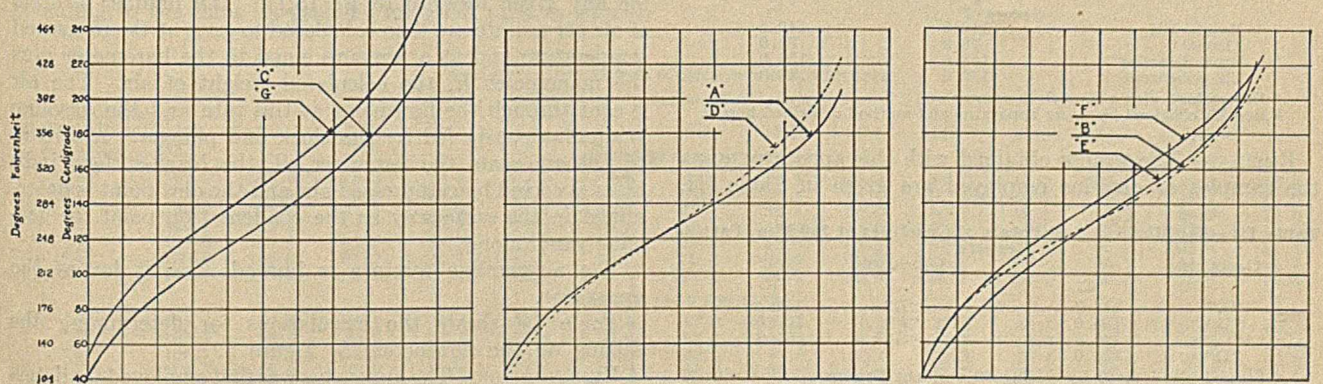

Figure 4—Engler Distillation Curves

librium that the liquid gasoline can be completely vaporized so quickly. The reason for this is not generally appreciated. A liquid droplet at a given temperature immediately forms a coating of vapor around it in equilibrium with the droplet. However, this coat of vapor smothers any further vaporization, and even if the temperature of the droplet increases, it only serves to increase the concentration of the vapor just around the droplet. Temperature alone is an inadequate means of vaporization, since it produces only spheroids or decomposes the gasoline. However, if this coating of vapor is removed, then the droplet immediately forms more vapor in its place. The time required to form vapor from a liquid is practically zero, so that the time required to vaporize a liquid into space is proportional only to the velocity with which the vapor is removed from the droplet into the space. The more rapidly this coating of vapor is removed the greater is the velocity of vaporization, the more nearly are the droplets in equilibrium with their environment the nearer the approximation to perfect equilibrium conditions. The heated screens offer excellent means for the rapid removal of the coating of vapor by the scrubbing of the vapor stream. In the presence of air this scrubbing effect is magnified, because there is acting as a brush not only the vapors but also the air. Therefore, approximate equilibrium conditions maintained by the coördination of heating with thorough and rapid mixing, permit the consummation of vaporization in a hundredth of a second in the manifold of an automobile.

The verification of this apparatus has also been demonstrated experimentally. A comparison of the results as determined by the phase-change method[5] and those obtained with this apparatus are given in Table I.

Table I—Equilibrium End Points at 760 Mm. Partial Pressure of Gasoline Vapor

Sample of Gasoline	Phase-Change Method	Black-Surface Method
	° C.	° C.
Socony 1925 "A"	150.0	152.3
	143.5	144.7
B. of S. "B"	153.4	154.0
B. of S. "C"	163.3	166.0
Stock 1925	157.9	160.0

These condensation points are in fact boiling points,[9] being the boiling points of the equilibrium solution. Table II shows how well this apparatus determines the boiling points of pure compounds.

Table II—Boiling Points and Equilibrium End Points of Pure Compounds

Compound	Boiling Point[a]	Equilibrium End Point[b]
	° C.	° C.
Xylol—EK	140.3	140.3
Alcohol	78.9	79.0
Bromobenzene	156.0	156.8
Chlorobenzene	132.0	132.0

[a] Determined with a B. of S. thermometer.
[b] Results obtained by using apparatus and method described herein.

Results—The results obtained with this apparatus upon the samples of gasoline employed are given in Table III.

Table III—Equilibrium End Points of Gasolines at 760 Mm. Partial Pressure

Gasoline		Gasoline	
	° C.		° C.
"A"	144.7	"E"	163.4
"B"	154.0	"F"	166.6
"C"	154.0	"G"[a]	191.9
"D"	154.0		

[a] Special blend made by mixing 80 per cent Socony gasoline with 20 per cent Socony kerosene.

The Engler distillation curves for these gasolines are given in Figure 4.

Discussion—Obviously the Engler curve and end point do not express the total volatility of a gasoline. The equilibrium end point represents by means of a single number this total volatility. The writers contend that the order of relative volatility that exists at 760 mm. partial pressure is the same as at 15 mm. partial pressure (within the range of automobile practice) and that even the quantitative differences are proportionately maintained with approximate accuracy.

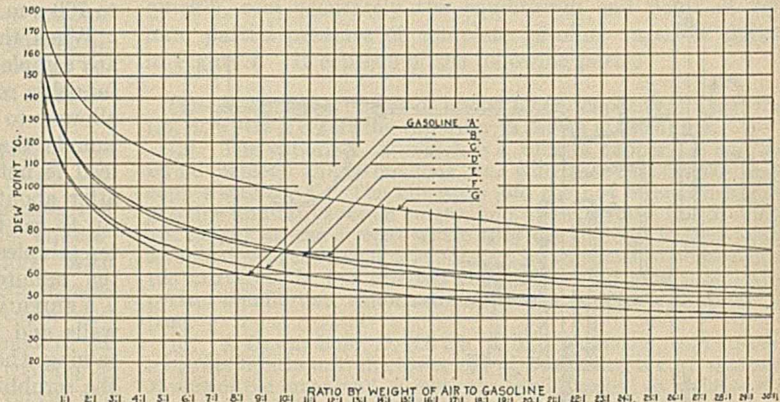

Figure 5—Relation between Dew Points of Gasoline-Air Mixtures and Equilibrium End Point of Gasoline Alone

Dew Points of Air-Gasoline Mixtures

Apparatus—The apparatus is shown in Figure 3. The device for vaporizing the gasoline and determining the dew point is the same as already described under Equilibrium End Point of Gasoline. The method of metering the air by flowmeter and the gasoline by a clock feed are the same as described by Sligh[7] except for the following modifications:

(1) The flowmeter, *L*, has a manometer tube that is parabolic in order to measure and maintain small as well as large velocities with equal precision.

(2) The gasoline container, *M*, is closed at the bottom with a mercury seal, *N*, to prevent leakage and contamination with stopcock grease. Another mercury seal, *O*, at the top prevents a loss of air and avoids the fractionation of the gasoline sample with the loss of its most volatile constituents by countercurrent evaporation. The use of the bent tube, *P*, insures a true sample of the gasoline taken from within the liquid and not from its surface. The tube *Q* equalizes the pressure and the water manometer, *R*, measures the total pressure.

Procedure—From the known rate of feed of the liquid gasoline and its specific gravity one calculates the weight of gasoline per minute and from that the weight of air needed for any given mixture (e. g., 15:1). The number of liters of air per minute are then calculated to give, at the measured temperature and at a pressure equal to the barometer plus the manometer *R*, the calculated weight of air. The air is sent through the flowmeter at this rate and the gasoline is simultaneously fed by the clock and plunger. A stream of hot air heats the vaporizer, *B*, the black-surface indicator is cooled by compressed air, and the dew point is determined in the same way as the condensation point for gasoline vapor alone.

The air-gasoline mixture is burned after it leaves the apparatus.

Table IV shows the calculations for determining the setting on the flowmeter, *L*, Figure 3.

Verification—The apparatus was first employed for determining the dew points of chlorobenzene and air and also bromobenzene and air. The liquid feed and the air feed

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[9] Young, "Stoichiometry," p. 137 (1908).

Table IV—Air Flowmeter Setting for Fuel "A"

Air Temperature at Intake	Barometric Pressure	Manometer Pressure	Total Actual Pressure in System	Volume Liquid Gasoline Fed	Sp. Gr. of Gasoline	Weight Gasoline Fed	Weight Ratio Air: Gasoline Desired	Air Desired	Wt. 1 Liter Dry Air under Actual Conditions	Air Desired under Actual Conditions
° C.	Mm. Hg	Mm. Hg	Mm. Hg	Cc./min.		Grams/min.		Grams/min.	Grams	Liters/min.
22	754.6	1.5	756.1	2.291	0.732	1.677	15:1	25.18	1.1904	21.15
22	753.8	0.4	754.2	2.291	0.732	1.677	6:1	10.06	1.1873	8.47

were adjusted to produce mixtures of air and vapor corresponding to the partial pressures of the vapor as given in the tables of Landolt-Börnstein. The dew points were determined as already explained with the black-surface dew indicator. The results are given in Table V. The temperatures from the Landolt-Börnstein tables are also given for comparison.

Table V—Dew Points of Mixtures of Chlorobenzene and Air and of Bromobenzene and Air

Substance	Vapor Pressure	Landolt-Börnstein	Dew Point
	Mm. Hg.	° C.	° C.
Chlorobenzene	26.68	40.0	38.2
	41.46	50.0	49.5
	64.74	60.0	60.6
Bromobenzene	16.92	50.0	50.3
	27.54	60.0	60.6
	43.31	70.0	70.0

Results—The experimental results for air-gasoline mixtures are given in Table VI. These results were plotted and the best curve was drawn for each gasoline, except that the results for gasolines "B," "C," and "D" are so nearly identical that one curve alone sufficed for the three gasolines (Figure 5). The corrected dew points as read from these curves are also given in Table VI.

There is a close correspondence with the experimental values.

Dew Points of Air-Gasoline Mixtures as Derived from Equilibrium End Point

The experimental determination of the dew points of the different air-gasoline mixtures within the range of use in an automobile is difficult and laborious. The determination of the equilibrium end point of the gasoline alone (760 mm. partial pressure) with the black-surface dew indicator is especially rapid, easy, and reliable. Therefore Figure 6 was constructed in order to test whether the dew points of the different air-gasoline mixtures of any particular gasoline could be inferred from the experimentally determined equilibrium end point of the gasoline itself. The existence of such a relationship between dew points and the equilibrium end point would be demonstrated if the dew points of any particular air-gasoline ratio for various gasolines lay on a smooth curve.

For each gasoline the corrected values given in Table VI were plotted against the equilibrium end point of that gasoline. All the points for the various gasolines corresponding to the same air-gasoline ratio fall upon a smooth curve. Thus the family of curves for the entire range of automobile operation was obtained. These curves are smooth and sensibly parallel. Figure 6 therefore expresses the relationship between the dew points and the equilibrium end point.

Obviously, for similar gasolines one may deduce with practical correctness the dew points of any air-gasoline mixture from the experimentally determined equilibrium end point of gasoline at 760 mm. partial pressure. Therefore, the writers propose the determination of this point by means of the black-surface dew indicator as the practical method for testing the volatility of gasolines. However, since the graph is empirical, the relation between the equilibrium end point of a fuel and the dew points of its air-fuel mixtures

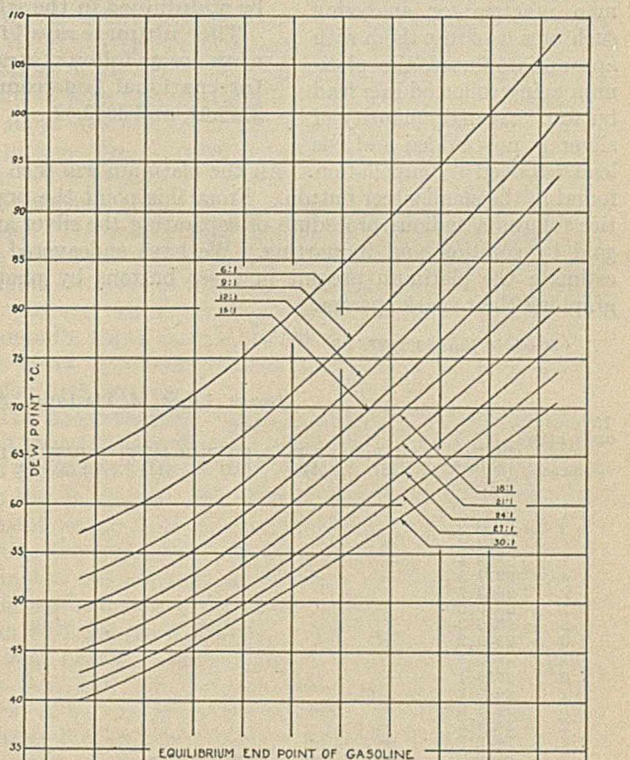

Figure 6

Table VI—Dew Points of Air-Gasoline Mixtures

(Dew points in degrees Centigrade)

Air-Gasoline Mixture Ratio	1:1	2:1	3:1	4:1	5:1	6:1	9:1	12:1	15:1	18:1	21:1	24:1	27:1	30:1
Gasoline						Experimental values								
"A"	107.2	90.0	78.3	72.8	68.9	65.6	59.4	53.9	48.3	46.7	45.0	44.4	42.2	40.6
"B"	105.6	91.1	83.3	78.3	72.8	69.4	63.3	58.3	54.4	51.7	49.4	47.8	46.1	45.0
"C"	108.9	95.6	85.6	78.9	73.3	69.4	62.2	58.3	55.0	50.0	49.4	47.8	46.7	45.0
"D"	106.7	93.3	85.6	78.9	73.3	70.6	61.1	58.3	55.0	51.7	49.4	47.8	46.1	45.0
"E"	123.9	100.6	91.7	86.7	81.1	76.7	69.4	65.0	61.1	57.2	56.1	55.0	53.3	52.2
"F"	120.0	105.6	97.2	91.1	84.4	77.2	72.8	68.9	62.8	60.0	58.9	56.1	53.3	51.7
"G"	146.7	128.9	123.3	117.2	112.2	108.3	101.1	94.4	89.4	83.3	81.1	76.7	73.3	70.0
						Values from Figure 5								
"A"	104.4	90.0	81.1	74.4	69.4	65.6	57.8	53.3	50.0	47.2	45.0	43.3	41.7	40.6
"B"	106.7	92.2	83.9	77.8	73.3	69.4	62.2	57.8	53.9	51.7	49.4	47.8	46.1	45.0
"C"	106.7	92.2	83.9	77.8	73.3	69.4	62.2	57.8	53.9	51.7	49.4	47.8	46.1	45.0
"D"	106.7	92.2	83.9	77.8	73.3	69.4	62.2	57.8	53.9	51.7	49.4	47.8	46.1	45.0
"E"	120.0	104.4	95.0	88.3	83.3	78.9	71.1	65.0	60.6	57.8	55.0	52.8	51.1	49.9
"F"	121.1	106.1	97.2	91.1	86.1	81.7	73.3	67.8	63.3	60.0	57.8	55.6	53.9	52.8
"G"	148.3	133.9	124.4	117.8	112.8	108.3	99.4	93.3	88.3	83.9	80.0	76.7	73.3	70.6

must be determined experimentally. Figure 6 applies to the commercial gasolines in the eastern section of the United States and probably with reasonable approximation to other gasolines.

Acknowledgment

This research was done at the expense of the Deppé Motors Corporation with the active coöperation of their chief engineer, Charles E. Parsons.

Spectroscopic Estimation of Platinum in Silver Alloys[1]

By Henry de Laszlo

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It is shown that platinum may be estimated quantitatively in silver beads with the aid of the spectrograph. The accuracy of the method may be increased by resorting to a simple form of photometry as indicated in the text, and by making up a larger number of standard silver-platinum alloys. Identical conditions must be maintained in the set-up.

The "ultimate rays" for the spark spectrum of platinum are as follows, arranged in order of sensitivity in International Ångström units: 3064.71, 2830.29, 3204.05, 2719.02, and 3042.62.

THE work reported herein was undertaken with a view to developing a quick and satisfactory method of determining platinum in its ores. The common practice for analyzing such ores is to fuse them with appropriate fluxes, the platinum being collected in a lead button. A small quantity of silver is now added and the lead removed by cupellation. All the platinum will then be found in the small silver button. From this point the practice follows a tedious procedure of separating the silver and gold by solution and inquarting. We have endeavored to estimate the platinum present in these buttons by photographing their spark spectra.

De Gramont[2] was the first to use the spectrograph for the quantitative estimation of metals in alloys. He studied the condensed spark spectra of alloys and mixtures of known compositions in which one particular metal was present in varying percentage concentrations and found that certain of the spark lines of that metal vanish as the concentration decreases. The last ones to disappear he designated as *raies ultimes* (ultimate rays). Each element has its own set of ultimate rays, a list of which has been published by de Gramont.[3]

Meggers, Kiess, and Stimson[4] have applied this method

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[1] Received June 29, 1927.

[2] *Rev. métal.* **19**, 90 (1922); *Ann. chim.*, **3**, 269 (1915).

[3] *Compt. rend.*, **171**, 1106 (1920).

[4] *Bur. Standards, Sci. Paper* **444**.

Spark Lines of Platinum Appearing in Platinum-Silver Alloys

INTENSITY OF Pt LINES IN 5% ALLOY	5% Pt (86)[a] Å.	2% Pt (58)	1% Pt (44)	0.5% Pt (32)	0.1% Pt (11)	0.02% Pt (5)	0.01% Pt (1)
1	2335.3						
2	2340.3						
4	2357.2	+	+				
2	2368.4	+					
4	2377.3	+	+				
2	2383.7						
1	2389.6						
2	2396.3						
3	2403.2	+					
1	2405.8						
2	2418.1	+					
1	2420.9						
5	2425.0	+	+	+			
2	2434.5	+					
3	2436.8	+	+				
7	2440.2	+	+	+	+		
2	2442.7						
2	2450.6	+					
1	2451.1						
6	2467.5	+	+	+			
8	2487.3	+	+	+			
1	2488.9						
4	2490.2	+					
4	2495.9	+	+	+			
5	2498.6	+	+	+			
2	2508.6	+					
2	2514.0	+					
1	2515.2						
5	2515.7	+	+	+			
2	2524.4						
3	2539.3	+					
3	2552.4						
1	2572.7						
1	2603.2						
10	2628.1	+	+	+	+		
2	2639.4	+	+				
9	2647.0	+	+	+			
8	2651.0	+	+	+			
15	2659.6	+	+	+	+		
1	2674.7						
3	2698.5	+	+				
13	2702.5	+	+	+	+		
11	2706.0	+	+	+			
10	2719.1	+	+	+	+	+	
4	2730.0	+	+				
13	2734.0	+	+	+	+		
1	2738.6						
1	2747.7						
2	2753.9						
6	2755.0	+	+	+			
1	2763.5						
9	2771.8	+	+	+			
6	2794.3	+	+	+			
2	2803.3						
13	2830.4	+	+	+	+	+	
2	2834.8						
1	2877.6						
8	2894.0	+	+				
6	2898.0	+	+	+			
2	2912.4	+	+				
3	2913.7	+	+	+			
3	2919.5						
10	2929.9	+	+	+			
1	2942.9						
2	2960.9	+					
12	2998.1	+	+	+	+		
5	3001.3	+					
7	3002.4	+	+	+			
8	3036.5	+	+				
10	3042.7	+	+	+	+	+	
15	3064.8	+	+	+	+	+	+
1	3072.1						
4	3100.1	+					
9	3139.5	+	+	+			
7	3156.7	+	+				
8	3200.9	+	+	+			
10	3204.2	+	+	+	+	+	
2	3252.1						
6	3256.1	+	+	+			
2	3290.4						
12	3302.0	+	+	+			
10	3408.3	+	+	+			
7	3485.4	+	+				
5	3628.3	+					
4	3818.8	+	+				
5	3923.1	+					

[a] Numbers in parenthesis are total number of lines.

to a number of alloys, among others to the estimation of iridium and rhodium in platinum. In the same paper they give an excellent account of the various methods of practical spectrographic analysis.

Our method consisted of the following steps:

(1) Several pairs of standard silver-platinum electrodes were prepared, each containing a definite amount of platinum ranging from 5 to 0.01 per cent.

(2) A condensed spark between each set of electrodes was photographed with a quartz spectrograph under identical conditions for a certain time.

(3) The spectra so obtained were measured and the number and wave length of the platinum lines visible in the spectrum of each alloy noted.

Preparation of Standard Electrodes

The alloys were made by two methods—cupellation as used in practice, and direct fusion on charcoal.

CUPELLATION—Silver foil of 99.95 per cent purity was weighed and wrapped around the required amount of platinum wire in such quantity that the resulting bead weighed about 200 mg. This bead was cupeled with lead in the ordinary way, the lead being removed by oxidation. Since there is always a tendency for the platinum-bearing silver to retain lead, the finishing temperature was kept higher than is necessary for pure silver. The beads were left in the furnace for about 10 minutes after solidification in order to remove as much lead as possible.

In making up the beads, there was a loss of silver varying between 1.2 to 2 per cent. The actual per cent is that computed from columns 3 and 4. The weight of the button is the weight after cupellation.

Electrodes Made by Cupellation

PLATINUM					
Normal	Actual	PLATINUM	SILVER	BUTTON	LOSS
Per cent	*Per cent*	*Mg.*	*Mg.*	*Mg.*	*Per cent*
5	5.05	10.10	189.64	196.66	1.5
	5.05	10.17	190.83	197.29	1.8
2	2.00	3.96	194.63	195.00	1.8
	2.00	2.56	125.14	126.00	1.2
1	1.00	1.91	188.78	187.95	1.4
	1.00	1.96	194.00	192.70	1.7
0.5	0.498	2.05	411.00	408.30	1.2
	0.499	0.85	170.30	168.08	1.8
0	...	...	201.16	198.33	1.4
	...	...	200.97	197.93	1.5

The resulting beads were cut in half, and the flat side of each hemisphere was soldered to a short piece of brass wire, thus forming a standard pair. Four pairs were made containing 5, 2, 1, and 0.5 per cent platinum. The presence of lead lines was noticed in the spectra of all beads prepared by cupellation. (The writer would like to thank L. B. Riley for his assistance in making up the alloys used in this work.) It was found that a 2 per cent platinum alloy and pure silver combination showed fewer platinum lines than two 0.1 per cent beads.

DIRECT FUSION—About 2 grams of a 0.1 per cent platinum alloy were made up by fusing weighed amounts of silver foil with platinum wire in a deep, narrow cavity in charcoal with the aid of a blowpipe. The resulting bead was rolled into a long, thin strip with annealing every few passes to prevent cracking. This strip was cut into five parts of about 400 mg. each. The two ends and center pieces were made up into three sets of electrodes which were compared spectroscopically with a set made by cupellation. There was no noticeable difference other than that the latter contained lead lines. This shows that the platinum was evenly distributed throughout the strip. The remaining two pieces were used to make 0.02 per cent and 0.01 per cent platinum alloys by weighing out the proper amount and fusing with pure silver on charcoal. These beads were mounted in the same way as the others. The silver loss amounted to only about 0.15 per cent for these alloys, there being no absorption loss and but little evaporation owing to the short time required for the fusion.

Photographing Spark Spectra

For the production of the spark spectra a Marconi $^1/_4$-kilowatt field set was used. This consists of a motor generator rating 110-volt d. c., 110-volt 300 ~ a. c. at 3000 r. p. m. The a. c. is transformed up to 10,000 volts in a small closed core transformer. The secondary circuit consisted of an adjustable spark gap to hold the standard electrodes, a Moscici condenser of 0.000638 microfarad, a self-induction coil of 0.0988 millihenry, and a rotating spark gap built onto the armature of the converter. This rotating spark gap insures great constancy for the light source, as the circuit is broken 600 times per second.

The distance between the electrodes was kept at 3 mm. The light of the spark was focused onto the slit of a Hilger quartz spectrograph (E_2) with the aid of a quartz lens of 45 mm. ϕ. The distance from spark to lens was 14 cm. and from lens to slit 70 cm. The slit width was 0.005 mm., the time of exposure for each set of alloys being 2 minutes. A Hartmann diaphragm was used on the slit. This consists of a slide with three holes of 3 mm. ϕ diagonally spaced on it. Thus, three photographs may be taken using different portions of the slit without moving the plate. A spark spectrum of pure platinum was photographed next to each pair of alloys with the aid of this diaphragm. This made it easy to pick out the platinum lines present in the alloy spectrum. The wave lengths of the platinum spark lines are given to one decimal place as no recent precision measurements exist. The values of Exner and Hascheks[5] are used and are sufficient for purposes of identification. The wave lengths are given in Ångström units and are neither reduced to vacuum nor international Ångströms. The Bureau of Standards hopes shortly to publish more accurate data on the spark spectrum of pure platinum in the ultra-violet region, 2000 to 2500 Å.

The accompanying table gives the list of platinum lines that were found in the 5 per cent alloy. The crosses denote the presence of the lines in question. Blanks indicate that the line is absent. By noting whether platinum lines are present in the spectrum of the unknown sample and consulting the table, one can tell what percentage of platinum is in the specimen to an accuracy of about 20 per cent. This method fails to be accurate with concentrations less than 0.04 per cent platinum. With the narrow slit used, we were unable to detect platinum lines in alloys containing less than 0.01 per cent platinum. By altering the conditions—i. e., increasing the slit width and the time of exposure—the method could be adapted to alloys with less than 0.01 per cent if that were necessary in practice.

Measurement of Ultimate Rays

To increase the accuracy of the method one should make some sort of photometric measurement of the ultimate rays corresponding to various platinum concentrations. Gerlach[6] has described this method very clearly, which in short is as follows:

> Let three or four lines, λ_1, λ_2, and λ_3, of the bulk of the alloy (in this case silver) be chosen near one of the ultimate rays λ_x of the impurity (platinum). If, then, we adopt these three lines as standards, we may perhaps find that the intensity of the impurity line at 1.0 per cent of platinum = λ_1, at 0.2 per cent platinum = λ_2, and 0.02 = λ_3. Then in analyzing the alloy the percentage impurity is determined by comparing the brightness of λ_x with λ_1, λ_2, or λ_3.

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[5] "Spektra der Elemente bei normalen Druck," and Kayser "Spektroscopie," Vol. 6.

[6] *Z. anorg. allgem. Chem.*, **142**, 387.

This method is independent of photographic effects, and could easily be applied to the above case.

The purpose of this paper is merely to give the necessary data with the aid of which a satisfactory method of routine platinum analysis could be worked out. This method could not, however, compete with the chemical methods in accuracy. A great deal of time would be saved, however, as the spectrograph would make possible an approximate determination in about half an hour as compared with the hours and days of the ordinary analytical procedure.

Formation of Hydrogen Sulfide by the Natural Reduction of Sulfates[1]

By L. Elion

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IN AN interesting article on the occurrence of hydrogen sulfide in the Lake Washington Ship Canal, Smith and Thompson[2] state that in the deeper portions of the canal system, where quantities of brackish water have accumulated, the presence of hydrogen sulfide has been noted. The authors conclude from their experiments that this hydrogen sulfide is produced by bacterial action upon the sulfates contained in the water. It appeared that the bacteria in question can adjust themselves to aerobic or anaerobic conditions and that, in the absence of dissolved oxygen, they begin to act upon salts containing chemically combined oxygen, such as sulfates.

To verify this explanation, Smith and Thompson refer mainly to investigations of Zelinsky[3] who studied the marked formation of hydrogen sulfide in the Black Sea, the chief cause of the thick layer of iron sulfide that covers the bottom. This Russian author reports the isolation of various microörganisms which had the power of evolving hydrogen sulfide from samples of the ooze of the Black Sea, while one of them, *Bacterium hydrosulfureum ponticum*, a facultative anaerobic microbe, was characterized by its remarkable power of producing hydrogen sulfide from sulfates, sulfites, etc.

In view of the prominent part biochemical sulfate reduction plays in nature, it seems of some interest to draw the attention to the fact, that not only is Zelinsky's bacterium entirely incompetent to attack sulfates, but that the bacterial capability of reducing these salts is generally misunderstood. In particular, the theory is often advanced that sulfate reduction, like denitrification, is a property possessed by many microörganisms, as reference to some well-known microbiological textbooks will disclose.[4]

As a matter of fact, however, although the quantity of hydrogen sulfide, owing its formation to the reduction of sulfates by living organisms is enormous, the number of true sulfate-reducing bacteria as yet isolated is only very small. Moreover, they are morphologically and physiologically very similar, but develop most favorably under somewhat different conditions. It is true that some very common bacteria are capable of forming hydrogen sulfide from protein, but it is necessary to discriminate between this process and the real sulfate reduction, which is of much more significance in nature.

Beijerinck[5] was the first to give an insight into the problem of the reduction of sulfates, and he recognized it as an oxidation of organic matter with the aid of the combined sulfate oxygen, according to the general equation:

$$2C + MeSO_4 + H_2O = MeCO_3 + CO_2 + H_2S$$

in which C designates the organic compound and Me a metal. It is clear that the energy required for the reduction is supplied by the combustion of the organic matter available.

Beijerinck also identified the bacterium in question, that was given the name *Spirillum* (afterwards *Microspira*) *desulfuricans*. It is a non-sporogenic, strictly anaerobic bacterium, as contrasted with the statements of Zelinsky and others, who described facultative anaerobic microörganisms.

Whereas Beijerinck's bacterium was isolated from ditch mud, van Delden[6] reported the presence of the same microbe in vegetable mold, Rank[7] in sea sand, and von Wolzogen Kühr[8] in the sand and clay beneath the Dutch dunes.

Van Delden, who cultivated this *Microspira desulfuricans* in pure culture, studied also the deposit of iron sulfide in the Wadden shallows near the Dutch coast and established that this salt resulted from the hydrogen sulfide produced from sulfates by a bacterium which he named *Microspira aestuarii*. Under the microscope both forms are identical, but *M. aestuarii*, which is also strictly anaerobic and non-sporogenic, possesses the remarkable differentiating property that a certain amount of sodium chloride is indispensable for its development.

Twenty years later the Russian investigator Issatchenko[9] confirmed van Delden's experiments in a new bacteriological study of the Black Sea and identified the microörganism isolated there with *M. aestuarii*. Certainly it will be of much interest to obtain pure cultures of the sulfate-reducing bacteria from the brackish waters of Lake Union, where similar conditions are prevailing.

Finally the writer[10] proved the existence of a third bacterium of this species, *Vibrio thermodesulfuricans*, morphologically indistinguishable from *M. desulfuricans* and *M. aestuarii* and also non-sporogenic and strictly anaerobic. This bacterium, however, is thermophilic, having its optimum temperature in the neighborhood of 55° C., whereas Beijerinck's and van Delden's bacteria flourish best at 25° to 30° C.

It is of interest that recently Bastin[11] and his collaborators discovered the importance of sulfate-reducing bacteria in the oil wells of Illinois and California. Many of the latter were characterized by rather high temperatures, 40° to 47° C. being not uncommon. It is not unlikely, therefore, that also in this case a thermophilic organism is concerned.

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[1] Received August 15, 1927.

[2] THIS JOURNAL, **19**, 822 (1927).

[3] *J. Russ. Phys. Chem. Soc.*, **25**, 298 (1893).

[4] Buchanan, "Agricultural and Industrial Bacteriology," p. 268; Marshall, "Microbiology," 3rd ed., p. 337.

[5] *Centr. Bakt. Parasitenk., II Abt.*, **1**, 1, 49, 104 (1895).

[6] *Centr. Bakt. Parasitenk., II Abt.*, **11**, 81, 113 (1904).

[7] Dissertation, Zürich, 1907.

[8] *Proc. Acad. Sci. Amsterdam*, **25**, 288 (1922).

[9] *Compt. rend.*, Paris, **178**, 2204 (1924).

[10] *Centr. Bakt. Parasitenk., II Abt.*, **63**, 58 (1924).

[11] *Bull. Am. Assocn. Petroleum Geol.*, **10**, 1270 (1926).

Assistant Commissioner of Patents Moore has affirmed the decision of the examiner of interferences that the marks "Zonite" and "Zonnox," both to be used on chemicals of the same descriptive properties, were dissimilar.

Recommended Specifications for Analytical Reagent Chemicals[1]

Molybdic Acid 85 Per Cent, Molybdic Acid Anhydride, Phosphoric Acid, Arsenic Trioxide, Barium Nitrate, Carbon Disulfide, Carbon Tetrachloride, Potassium Phosphate Monobasic, Sodium Nitrate, Sodium Peroxide, Sodium Phosphate Dibasic, Sodium Sulfide, Stannous Chloride

By W. D. Collins, H. V. Farr, Joseph Rosin, G. C. Spencer, and Edward Wichers

COMMITTEE ON ANALYTICAL REAGENTS, AMERICAN CHEMICAL SOCIETY

The specifications given below are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications[2] from the committee. Directions for the preparation of the ammonium molybdate solution are given under the test for phosphate in ammonium nitrate.[3] A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Acid, Molybdic, 85 Per Cent

Note—This reagent, commonly known as "acid molybdic, 85 per cent" consists largely of ammonium molybdate.

REQUIREMENTS

Assay—Not less than 85 per cent MoO_3.
Insoluble in Ammonium Hydroxide—Not more than 0.010 per cent.
Chloride (Cl)—Not more than 0.005 per cent.
Phosphate (PO_4)—Not more than 0.0005 per cent.
Sulfate (SO_4)—Not more than 0.20 per cent.
Heavy Metals (as lead)—Not more than 0.005 per cent.

TESTS

Assay—Weigh accurately about 0.5 gram and dissolve with heat in a mixture of 50 cc. of water and 3 cc. of dilute ammonium hydroxide (1 + 2). Add 5 cc. of acetic acid (1 + 2), dilute to 200 cc., heat to boiling, and add a clear solution of 1.5 gram of lead acetate crystals in 20 cc. of water; boil for several minutes with stirring till the precipitate becomes granular and settles readily. Decant the supernatant liquid through ignited asbestos in a Gooch crucible, wash the precipitate by decantation ten times with 50 cc. portions of boiling water; transfer the precipitate to the crucible, dry, ignite, and weigh as $PbMoO_4$.

Insoluble in Ammonium Hydroxide—Dissolve 10 grams in a mixture of 25 cc. of water and 10 cc. of ammonium hydroxide. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the insoluble residue should not exceed 0.0010 gram. Save the filtrate separate from the washings.

Chloride—Digest 1.5 grams with 20 cc. of water and 10 cc. of nitric acid for 15 minutes and filter. To 20 cc. of the filtrate add 1 cc. of 0.1 N silver nitrate solution. The turbidity should not be greater than is produced by 0.05 mg. of chloride ion in 15 cc. of water and 5 cc. of nitric acid with 1 cc. of 0.1 N silver nitrate solution.

Phosphate—Pour the filtrate (without the washings) obtained in the test for insoluble matter into a mixture of 50 cc. of nitric acid and 75 cc. of water. Shake for 5 minutes (at 40° C.) and allow to stand 1 hour. Any precipitate should not be greater than is produced by 0.05 mg. of phosphate (PO_4) under the same conditions.

Sulfate—Boil 1 gram with a mixture of 10 cc. of water and 5 cc. of nitric acid for 5 minutes. Cool thoroughly, dilute to 50 cc., mix well, and filter. Evaporate 10 cc. of the filtrate to dryness on the steam bath, warm the residue with 3 drops of hydrochloric acid and 10 cc. of water, filter if necessary, wash, make the filtrate to 50 cc., and add 1 cc. of 10 per cent barium chloride solution. Any turbidity should not be greater than is produced by 0.4 mg. of sulfate ion in the same volume of solution containing the quantities of acid and barium chloride used in the test.

Heavy Metals—Dissolve 1 gram in 15 cc. of 10 per cent sodium hydroxide solution, add 2 cc. of ammonium hydroxide, and dilute to 50 cc. To 10 cc. of the diluted solution add 3 cc. of hydrogen sulfide water. Any brown color should not be greater than is produced by 0.01 mg. of lead in an alkaline sulfide solution.

Acid, Molybdic Anhydride

REQUIREMENTS

Assay—Not less than 99.5 per cent.
Insoluble in Ammonium Hydroxide—Not more than 0.010 per cent.
Chloride (Cl)—Not more than 0.002 per cent.
Nitrate (NO_3)—To pass test (limit about 0.003 per cent).
Phosphate (PO_4)—Not more than 0.0005 per cent.
Sulfate (SO_4)—Not more than 0.002 per cent.
Heavy Metals (as lead)—Not more than 0.005 per cent.
Ammonia—Not more than 0.010 per cent.

TESTS

Assay—Use method for Acid, Molybdic, 85 per cent.

Insoluble in Ammonium Hydroxide—Use method for Acid Molybdic, 85 per cent.

Chloride—Use method for Acid, Molybdic, 85 per cent, but compare with 0.02 mg. of chloride ion.

Nitrate—Triturate 1 gram with 10 cc. of water, add about 5 mg. of sodium chloride, 2 drops of indigo solution (1 in 1000), and 10 cc. of sulfuric acid. The blue color should not be entirely discharged in 5 minutes.

Phosphate—Use method for Acid, Molybdic, 85 per cent.

Sulfate—Boil 3 grams with a mixture of 10 cc. of nitric acid and 20 cc. of water for 5 minutes. Cool, dilute to 45 cc., mix well, and filter. Evaporate 30 cc. of the filtrate to dryness on the steam bath, warm the residue with 2 drops of hydrochloric acid and 10 cc. of water, filter if necessary, and add 1 cc. of 10 per cent barium chloride. The turbidity after 15 minutes should not be greater than is produced by 0.04 mg. of sulfate radical in 10 cc. of water with 2 drops of hydrochloric acid and 1 cc. of barium chloride.

Heavy Metals—Use method for Acid, Molybdic, 85 per cent.

Ammonia—Dissolve 0.5 gram in 10 cc. of 10 per cent sodium hydroxide, dilute to 50 cc., and add 3 cc. of Nessler's solution. The color should not be greater than is produced by a quantity of an ammonium salt containing 0.05 mg. of ammonia in a volume of 50 cc. containing 10 cc. of the sodium hydroxide on the addition of 3 cc. of Nessler's solution.

Acid, Phosphoric

REQUIREMENTS

Assay—Not less than 85 per cent H_3PO_4.
Chloride (Cl)—Not more than 0.0005 per cent.
Nitrate (NO_3)—To pass test (limit about 0.0005 per cent).
Reducing Substances—To pass test.
Sulfate (SO_4)—Not more than 0.003 per cent.
Volatile Acids (as acetic)—Not more than 0.0015 per cent.
Alkali and Other Phosphates—Not more than 0.20 per cent as sulfates.
Arsenic (As)—Not more than 0.0002 per cent.
Heavy Metals—Not more than 0.001 per cent as lead.
Iron—Not more than 0.005 per cent.

TESTS

Assay—Weigh accurately about 1 cc., dilute with 25 cc. of water, and dissolve in the solution about 5 grams of pure sodium chloride. Cool the solution o about 15° C. and titrate at this temperature with normal alkali, using 3 drops of phenolphthalein indicator solution.

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[1] Presented in connection with the report of the Committee on Analytical Reagents at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] THIS JOURNAL, **17**, 756 (1925); **18**, 636, 759 (1926); **19**, 645 (1927).

[3] *Ibid.*, **19**, 645 (1927).

Chloride—Dilute 3 cc. (5 grams) with water to 25 cc. and add 1 cc. of 0.1 *N* silver nitrate. Any turbidity produced should not be greater than is produced by 0.025 mg. of chloride ion in an equal volume of water acidified with nitric acid and containing 1 cc. of 0.1 *N* silver nitrate.

Nitrate—Dilute 2 cc. to 10 cc., add 5 mg. of sodium chloride, 1 drop of indigo solution (1 in 1000), and 10 cc. of sulfuric acid. The blue color should not be discharged in 10 minutes.

Reducing Substances—Dilute 10 cc. with 5 cc. of water, add 0.20 cc. of 0.1 *N* potassium permanganate, heat just to boiling, and allow to stand on the steam bath for 10 minutes. The pink color should not be entirely discharged.

Sulfate—Dilute 12 cc. (20 grams) with 190 cc. of water, boil, add 10 cc. of 10 per cent barium chloride solution, allow to stand overnight, filter, wash, ignite, and weigh. The weight of the barium sulfate should not exceed 0.0015 gram.

Volatile Acids—Dilute 25 cc. with 75 cc. of water free from carbon dioxide and distil off 50 cc. The distillate should not require more than 0.1 cc. 0.1 *N* sodium hydroxide for neutralization, using 3 drops of phenolphthalein indicator solution.

Alkali and Other Phosphates—Dissolve 3 grams in 100 cc. of water, add a solution of 15 grams of lead acetate in 50 cc. of water, and make up to 200 cc. Filter off 100 cc. and pass hydrogen sulfide through the filtrate to precipitate the lead. Filter and wash with 20 cc. of water. Add to the filtrate 2 drops of sulfuric acid, evaporate to dryness, ignite gently, and weigh. The weight should not be more than 0.0030 gram after correction for the blank on the lead acetate.

Arsenic—Determine on a 2-gram sample by the modified Gutzeit method.

Heavy Metals—Dilute 3 cc. with 30 cc. of water, neutralize to litmus with ammonium hydroxide, add 1 cc. of hydrochloric acid and 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color should not be greater than is produced under the same conditions by 0.05 mg. of lead.

Iron—Dilute 3 cc. to 100 cc., take 5 cc. of this solution and dilute to 40 cc. Add 2 cc. of ammonium hydroxide and 5 cc. of hydrogen sulfide water. Any green color should not be greater than is produced by 0.0125 mg. of iron under the same conditions.

Arsenic Trioxide (a primary standard)

Requirements

Non-volatile Matter—Not more than 0.020 per cent.

Insoluble in Ammonium Hydroxide—Not more than 0.010 per cent.

Chloride (Cl)—Not more than 0.005 per cent.

Sulfide (S)—To pass test (limit about 0.001 per cent).

Antimony and Other Hydrogen Sulfide Metals—To pass test (limit about 0.002 per cent antimony; about 0.001 per cent lead).

Iron—Not more than 0.0005 per cent.

Tests

Non-volatile Matter—Ignite 5 grams under the hood and weigh the residue. The weight should not exceed 0.0010 gram.

Insoluble in Ammonium Hydroxide—Heat 5 grams with 50 cc. of dilute ammonium hydroxide (1 + 2) in an Erlenmeyer flask with a reflux condenser till the sample is dissolved. Filter through asbestos in a Gooch crucible, wash with warm dilute ammonium hydroxide, dry at 105° to 110° C., and weigh. The weight of the insoluble residue should not exceed 0.0005 gram.

Chloride—Dissolve 1 gram in 10 cc. of dilute ammonium hydroxide (1 + 2) by heating, cool, add an excess of dilute nitric acid and 2 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.05 mg. of chloride ion in an equal volume of solution containing approximately the quantities of reagents used in the test.

Sulfide—Dissolve 1 gram in 10 cc. of *N* sodium hydroxide solution and add 1 drop of lead acetate solution. The color should be the same as that of an equal volume of the sodium hydroxide solution to which only the lead acetate is added.

Antimony and Other Hydrogen Sulfide Metals—Dissolve 1 gram in 10 cc. of hydrochloric acid and 10 cc. of water. Evaporate to dryness, take up in 2 cc. of acid and 2 cc. of water, and evaporate again. Take up with 1 cc. of hydrochloric acid, dilute to 10 cc., neutralize with ammonium hydroxide, add 1 cc. of *N* hydrochloric acid and 10 cc. of hydrogen sulfide water. No color should be produced.

Iron—Dissolve 1 gram in 5 cc. of hydrochloric acid, dilute to 20 cc., and add liquid bromine a little at a time till the bromine color is permanent. Boil off the excess of bromine, dilute to 20 cc., cool, and add 1 cc. of 10 per cent ammonium thiocyanate solution. Any red coloration should not be greater than is produced by 0.005 mg. of iron in the same volume of solution with the quantities of reagents used in the test.

Barium Nitrate

Requirements

Insoluble Matter—Not more than 0.010 per cent.

Chloride (Cl)—Not more than 0.0005 per cent.

Calcium and Alkali Salts—Not more than 0.050 per cent as sulfates.

Calcium and Strontium Salts—Not more than 0.10 per cent as chlorides.

Heavy Metals—To pass test (limit about 0.0005 per cent lead).

Iron—To pass test (limit about 0.0002 per cent).

Tests

Insoluble Matter—Dissolve 10 grams in about 100 cc. of hot water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water, add 2 drops of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.005 mg. of chloride ion in an equal volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Calcium and Alkali Salts—Dissolve 5 grams in about 150 cc. of water, add 1 cc. of hydrochloric acid, and heat to boiling. Add 25 cc. of 2 *N* sulfuric acid, cool, make up to 250 cc., and allow to stand overnight. Decant through a dry filter, evaporate 100 cc. of the filtrate to dryness, ignite, and weigh. The weight of the residue should not exceed 0.0010 gram.

Calcium and Strontium Salts—Dissolve 2 grams in 15 cc. of hot water, add 10 cc. of hydrochloric acid, and evaporate to dryness on the steam bath. Dissolve the residue in 10 cc. of hot water, add 10 cc. of hydrochloric acid, evaporate to dryness again, and dry in the oven at 105° C. Grind the residue to a fine powder, and treat with 20 cc. of absolute alcohol. Allow to stand for 30 minutes with occasional shaking, filter, evaporate the filtrate, ignite gently, and weigh. The weight of the residue should not exceed 0.0020 gram.

Heavy Metals—Dissolve 2 grams in 40 cc. of water, add 0.5 cc. of glacial acetic acid and 10 cc. of hydrogen sulfide water. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution tested for heavy metals till it is alkaline to litmus. No green color should be produced.

Carbon Disulfide

Requirements

Boiling Range—46° to 47° C.

Non-volatile Matter—Not more than 0.002 per cent.

Foreign Sulfides—To pass test.

Sulfite and Sulfate—To pass test (limit about 0.002 per cent SO_2).

Water—To pass test.

Tests

Boiling Range—Distil 100 cc., immersing the bulb of the distilling flask in water heated to about 60° C.

Non-volatile Matter—Evaporate 40 cc. at 50° to 60° C. The residue should not have a disagreeable odor. Dry for 1 hour at 60° C. and weigh. The weight of the residue should not exceed 0.0010 gram.

Foreign Sulfides—Shake 2 cc. in a dry test tube with a globule of mercury for 2 minutes. The mercury should remain bright.

Sulfite and Sulfate—Shake 10 cc. with 10 cc. of water in a separatory funnel for 5 minutes; separate and discard the carbon disulfide. To the aqueous layer add 1 drop of 0.1 *N* iodine solution. A yellow or violet color should be produced. Add to the solution 1 cc. of 10 per cent barium chloride solution. No turbidity should be produced in 15 minutes.

Water—Cool 10 cc. in a test tube to 0° C. No turbidity or drops of water should appear.

Carbon Tetrachloride

Requirements

Boiling Point—76° to 78° C.

Non-volatile Matter—Not more than 0.001 per cent.

Acid—To pass test.

Aldehyde—To pass test.

Chloride—Not more than 0.0002 per cent.

Free Chlorine—To pass test.

Iodine-Consuming Substances—To pass test.

Substances Darkened by Sulfuric Acid—To pass test.

Sulfur Compounds (as S)—Not more than 0.005 per cent.

Tests

Boiling Point—Determine by the method of the U. S. Pharmacopeia. When the directions are followed 95 per cent of the sample tested must come over within the temperature range indicated.

Non-volatile Matter—Evaporate 60 cc. on the steam bath and dry at 105° to 110° C. for half an hour. The weight of the residue should not exceed 0.0010 gram.

Acid—Shake 13 cc. with 20 cc. of water for 5 minutes, separate and reject the carbon tetrachloride. Add to 10 cc. of the aqueous layer 2 drops of phenolphthalein indicator solution and 0.05 cc. of *N* sodium hydroxide. A pink color should be produced.

Aldehyde—Shake 10 cc. with 10 cc. of water containing 0.05 cc. of 0.1 *N* potassium permanganate. The color should not disappear in 5 minutes.

Chloride—To 10 cc. of the aqueous layer from the test for acid add 2 drops of nitric acid and 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity should not be greater than is produced by 0.02 mg. of chloride ion in 10 cc.

of water upon the addition of the quantities of acid and silver nitrate used in the test.

Free Chlorine—Shake 10 cc. for 2 minutes with 10 cc. of water to which 2 drops of 10 per cent potassium iodide has been added and allow to separate. The lower layer should not show a violet tint.

Iodine-Consuming Substances—To 25 cc. add 1 drop of 0.1 *N* iodine solution and shake well. The violet color should remain at the end of 30 minutes.

Substances Darkened by Sulfuric Acid—Shake 20 cc. with 5 cc. of sulfuric acid for 5 minutes in a glass-stoppered cylinder which has been rinsed with sulfuric acid. After the layers have separated the sulfuric acid should show not more than a slight yellow color.

Sulfur Compounds—To 3 cc. in an Erlenmeyer flask add 30 cc. of approximately 0.5 *N* alcoholic potassium hydroxide solution and boil the mixture gently for 30 minutes under a reflux condenser. Detach the condenser, dilute with 50 cc. of water, and heat on the steam bath till the carbon tetrachloride and alcohol are evaporated. Add 50 cc. of saturated bromine water and heat for 15 minutes longer. Transfer the solution to a beaker, neutralize with hydrochloric acid, add an excess of 1 cc. of the acid, and concentrate to about 50 cc. Filter if necessary, heat the filtrate to boiling, add 5 cc. of 10 per cent barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate forms, filter, wash, ignite, and weigh. The weight of barium sulfate should not exceed 0.0020 gram after correction is made for sulfur in the reagents used.

Potassium Phosphate, Monobasic (Potassium Dihydrogen Phosphate)

Requirements

Insoluble, Calcium, and Ammonium Hydroxide Precipitate—Not more than 0.010 per cent.

Loss on Drying over Sulfuric Acid—Not more than 0.20 per cent.

Loss on Ignition (proof of proper composition)—Between 13.15 and 13.35 per cent.

Hydrogen-Ion Concentration (as pH)—To pass test.

Chloride (Cl)—Not more than 0.001 per cent.

Nitrogen Compounds (as N)—Not more than 0.001 per cent.

Sulfate (SO_4)—To pass test (limit about 0.003 per cent).

Heavy Metals—Not more than 0.001 per cent as lead.

Iron (Fe)—Not more than 0.002 per cent.

Sodium (Na)—To pass test (limit about 0.03 per cent).

Tests

Insoluble, Calcium, and Ammonium Hydroxide Precipitate—Dissolve 10 grams in 100 cc. of water, add 5 cc. of 4 per cent ammonium oxalate solution, and add ammonium hydroxide till the solution is distinctly alkaline to litmus. Add an excess of 15 cc. of ammonium hydroxide and allow to stand overnight. If any precipitate is formed, filter, wash, ignite at a low red heat, and weigh. The weight should not exceed 0.0010 gram.

Loss on Drying over Sulfuric Acid—Accurately weigh about 2 grams and dry for 24 hours over sulfuric acid. The loss in weight should not exceed 0.20 per cent.

Loss on Ignition—Ignite carefully to constant weight the dried residue obtained in the preceding test. The loss in weight should be not less than 13.15 per cent and not more than 13.35 per cent.

Hydrogen-Ion Concentration—Prepare a 0.2 *M* solution and determine the pH by the use of indicators or electrometrically. The pH should lie between 4.4 and 4.7. Take 10-cc. portions of the solution in four test tubes and to each of two add 5 drops of a 0.04 per cent solution of bromphenol blue. To each of the other two add 5 drops of a 0.02 per cent solution of methyl red. To one tube with the bromphenol blue add 0.05 cc. of 0.1 *N* hydrochloric acid and to one of the tubes with methyl red add 0.05 cc. of 0.1 *N* sodium hydroxide. The solutions in the tubes to which acid and alkali are added should show distinct changes of color when compared with the corresponding tubes to which neither acid nor alkali was added.

Chloride—Dissolve 2 grams in 20 cc. of water, add 2 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity produced should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of distilled water on the addition of the quantities of acid and silver nitrate used in the test.

Nitrogen Compounds—Dissolve 2 grams in 30 cc. of water, add 20 cc. of 10 per cent sodium hydroxide solution and 0.5 gram of aluminum wire in small pieces. Allow to stand for 3 hours protected against loss or access of ammonia, decant 25 cc., and add 2 cc. of Nessler's solution. Any color should not be greater than is produced by a quantity of an ammonium salt containing 0.01 mg. of nitrogen (N). Correction must be made for any nitrogen in the reagents used.

Sulfate—Dissolve 10 grams in 100 cc. of water, add 1 cc. of hydrochloric acid, and heat to boiling. Add 5 cc. of 10 per cent barium chloride and allow to stand overnight. No precipitate should be formed.

Heavy Metals—Dissolve 5 grams in 40 cc. of water, neutralize to litmus with ammonium hydroxide, add 1 cc. of hydrochloric acid and 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color should not be greater than is produced by 0.05 mg. of lead under the same conditions.

Iron—Dissolve 5 grams in 100 cc. of water, take 5 cc. of this solution and dilute to 40 cc., add 2 cc. of ammonium hydroxide and 5 cc. of hydrogen sulfide water. Any green color should not be greater than is produced by 0.005 mg. of iron under the same conditions.

Sodium—A 10 per cent solution tested on a platinum wire in the flame should impart no distinct yellow color to the flame.

Sodium Nitrate

Requirements

Insoluble Matter—Not more than 0.005 per cent.

Neutrality—To pass test.

Chlorine, Total—Not more than 0.001 per cent.

Iodate, Nitrite—To pass test (limit about 0.0005 per cent IO_3, about 0.001 per cent NO_2).

Phosphate (PO_4)—Not more than 0.0005 per cent.

Sulfate (SO_4)—Not more than 0.003 per cent.

Calcium and Magnesium Precipitate—Not more than 0.005 per cent.

Heavy Metals—To pass test (limit about 0.0005 per cent lead).

Iron (Fe)—Not more than 0.0003 per cent.

Tests

Insoluble Matter—Dissolve 10 grams in 50 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0005 gram.

Neutrality—Dissolve 5 grams in 50 cc. of water free from carbon dioxide and add 3 drops of phenolphthalein. No pink color should be produced, but on the addition of 1 drop of 0.1 *N* sodium hydroxide a pink color should be produced.

Chlorine, Total—Ignite 1 gram, at first gently and then for a few minutes at a low red heat. Cool, dissolve in 20 cc. of water, add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.01 mg. of chloride ion under the same conditions.

Iodate, Nitrite—Dissolve 1 gram in 10 cc. of water, add 2 drops of 10 per cent potassium iodide, 1 cc. of chloroform, and 2 cc. of 36 per cent acetic acid. Shake gently for a few minutes. The chloroform should not acquire a pink or violet color.

Phosphate—Dissolve 5 grams in 50 cc. of water, add 10 cc. of nitric acid, and nearly neutralize with ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake (at about 40° C.) for 5 minutes, and allow to stand one-half hour. Any precipitate formed should not be greater than is produced when a quantity of an alkali phosphate containing 0.025 mg. of phosphate (PO_4) is treated according to the above procedure.

Sulfate—Dissolve 12 grams in 20 cc. of water, add 25 cc. of hydrochloric acid and evaporate to dryness. Treat the residue with 15 cc. of water and 15 cc. of hydrochloric acid, and again evaporate to dryness. Dissolve the residue in 75 cc. of water, add 1 cc. of 10 per cent hydrochloric acid, heat to boiling, add 5 cc. of 10 per cent barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If any precipitate is formed, filter, wash, ignite, and weigh. The weight of the barium sulfate should not exceed 0.0010 gram.

Calcium and Magnesium Precipitate—Dissolve 10 grams in 75 cc. of water, add 5 cc. of 4 per cent ammonium oxalate, 2 cc. of 10 per cent ammonium phosphate, and 15 cc. of ammonium hydroxide, and allow to stand overnight. If any precipitate forms, filter, wash, ignite, and weigh. The weight of the ignited precipitate should not exceed 0.0005 gram.

Heavy Metals—Dissolve 2 grams in 20 cc. of water and add 10 cc. of hydrogen sulfide water. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution tested for heavy metals till it is alkaline. Any greenish color should not be greater than is produced by 0.006 mg. of iron in an alkaline sulfide solution.

Sodium Peroxide

Requirements

Assay—Not less than 90 per cent Na_2O_2.

Chloride (Cl)—Not more than 0.002 per cent.

Nitrogen Compounds (as N)—Not more than 0.003 per cent.

Phosphate (PO_4)—Not more than 0.0005 per cent.

Sulfate (SO_4)—Not more than 0.001 per cent.

Heavy Metals—Not more than 0.002 per cent as lead.

Iron (Fe)—Not more than 0.003 per cent.

Tests

Assay—Weigh carefully about 0.7 gram and add slowly to a mixture of 400 cc. of water and 5 cc. of sulfuric acid which has been cooled to 10° C. Dilute to 500 cc., mix well, and titrate 100 cc. with 0.1 *N* permanganate solution.

Chloride—Add 1 gram in small portions to 20 cc. of water, cool and add 5 cc. of nitric acid. Filter if necessary and add 1 cc. of 0.1 *N* silver nitrate. Any turbidity produced should not be greater than is produced by 0.02 mg. of chloride ion under similar conditions.

Nitrogen Compounds—Dissolve 1 gram in 20 cc. of water cooled with ice, add acetic acid till neutral, add an excess of 3 drops, and boil down to a volume of 10 cc. Cool, dilute with 25 cc. of water, add 20 cc. of 10 per cent sodium hydroxide solution and 0.5 gram of aluminum wire in small pieces, and allow to stand 3 hours protected against loss or access of ammonia. Decant 25 cc. of the clear liquid and add to it 2 cc. of Nessler's solution. Any color should not be greater than that obtained by treating a quantity of a nitrate containing 0.030 mg. of nitrogen (N) exactly as the 1 gram of sample was treated.

Phosphate—Cautiously add 5 grams to a cooled mixture of 12 cc. of nitric acid and 50 cc. of water and evaporate to dryness on the steam bath. Take up in 50 cc. of water and 5 cc. of nitric acid, and nearly neutralize the acid with ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake (at about 40° C.) for 5 minutes, and allow to stand one-half hour. Any precipitate formed should not be greater than is produced when a quantity of an alkali phosphate containing 0.025 mg. of phosphate (PO_4) is treated according to the above procedure.

Sulfate—Dissolve 20 grams in 150 cc. of water, boil down to about 90 cc., cool, neutralize with hydrochloric acid, and add an excess of 1 cc. Filter if necessary, heat the filtrate to boiling, add 5 cc. of 10 per cent barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate is formed, filter, wash, ignite, and weigh. The weight of the ignited precipitate should not exceed 0.0005 gram.

Heavy Metals—Carefully add 2 grams to a mixture of 5 cc. of hydrochloric acid and 15 cc. of water and evaporate to dryness on the steam bath. Take up the residue in 25 cc. of water and pass hydrogen sulfide through the solution. Any brown color should not be greater than is produced by 0.04 mg. of lead under the same conditions.

Iron—Carefully add 1 gram to a mixture of 2 cc. of nitric acid and 10 cc. of water and evaporate to dryness. Treat the residue with 2 cc. of hydrochloric acid and 10 cc. of water, warming slightly. Cool, dilute to 20 cc. and add 1 cc. of 10 per cent ammonium thiocyanate. Any red color should not be greater than is produced by 0.03 mg. of ferric iron under the same conditions.

Sodium Phosphate, Dibasic (Disodium Hydrogen Phosphate)

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.
Neutrality—To pass test.
Chloride (Cl)—Not more than 0.001 per cent.
Nitrogen Compounds (as N)—Not more than 0.001 per cent.
Sulfate (SO_4)—Not more than 0.010 per cent.
Arsenic (As)—Not more than 0.0005 per cent.
Heavy Metals—To pass test (limit 0.001 per cent as lead).
Iron (Fe)—Not more than 0.001 per cent.

TESTS

Insoluble Matter—Dissolve 10 grams in 100 cc. of water, allow to stand on the steam bath for 1 hour, filter through asbestos in a Gooch crucible, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram.

Neutrality—Dissolve 3 grams in 30 cc. of water at 15° C. and add 3 drops of phenolphthalein solution. A red color should be produced which should be discharged by the addition of 0.6 cc. of *N* hydrochloric acid. Boil the solution for 2 minutes, cool to 15° C., and dilute to the original volume with cold water. No pink color should appear.

Chloride—Dissolve 2 grams in 20 cc. of water, add 3 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of solution with the quantities of acid and silver nitrate used in the test.

Nitrogen Compounds—Dissolve 2 grams in 30 cc. of water, add 20 cc. of 10 per cent sodium hydroxide solution and 0.5 gram of aluminum wire in small pieces. Allow to stand for 3 hours protected from loss or access of ammonia. Decant 25 cc. of the clear liquid and add 2 cc. of Nessler's solution. The color should not be more than is produced in a similar aliquot of a solution obtained by treating a quantity of an ammonium salt containing 0.02 mg. of nitrogen with the quantity of water and reagents used in the test.

Sulfate—Dissolve 10 grams in 100 cc. of water, add 5 cc. of hydrochloric acid and heat to boiling. Add 5 cc. of 10 per cent barium chloride, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate forms, filter, wash, ignite, and weigh. The weight of the ignited barium sulfate should not exceed 0.0025 gram.

Arsenic—Determine on a 2 gram sample by the modified Gutzeit method.

Heavy Metals—Dissolve 5 grams in 40 cc. of water, render neutral to litmus paper, add 1 cc. of hydrochloric acid and 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color should not be more than is produced by 0.05 mg. of lead in the same volume of a solution containing the quantities of hydrogen sulfide and excess hydrochloric acid used in the test.

Iron—Dissolve 5 grams in 100 cc. of water. Dilute 10 cc. of the solution to 40 cc., add 1 cc. of ammonium hydroxide and 5 cc. of hydrogen sulfide water. Any green color should not be greater than is produced by 0.005 mg. of iron in an equal volume of alkaline solution when 5 cc. of hydrogen sulfide water are added.

Sodium Sulfide

REQUIREMENTS

Appearance—Crystals, colorless or with no more than a slight yellow color.
Ammonium Compounds (as N)—Not more than 0.002 per cent.
Sulfite, Thiosulfate—To pass test (limit about 0.10 per cent SO_2).
Iron (Fe)—To pass test.

TESTS

Ammonium Compounds—Dissolve 2 grams in 80 cc. of water, add a solution of 3.5 grams of lead acetate in 20 cc. of water, and allow the precipitate to settle. Decant 50 cc., add an excess of sodium hydroxide and water to make 100 cc. Distil off 50 cc. and add to the distillate 2 cc. of Nessler's solution. The color should not be more than is produced by a quantity of an ammonium salt containing 0.02 mg. of nitrogen, after correction is made for nitrogen in the lead acetate, sodium hydroxide, and water used in the test.

Sulfite, Thiosulfate—Dissolve 3 grams in 200 cc. of water free from oxygen and add a solution of 5 grams of zinc sulfate in 100 cc. of water free from oxygen. Shake well, allow to stand half an hour, filter, and titrate 100 cc. of the filtrate with 0.1 *N* iodine solution, using starch indicator. Not more than 0.3 cc. of the iodine solution should be required.

Iron—Dissolve 5 grams in 100 cc. of water. The solution should be clear and colorless.

Stannous Chloride

REQUIREMENTS

Solution—To pass test.
Sulfate (SO_4)—To pass test (limit about 0.003 per cent).
Arsenic (As)—To pass test (limit about 0.0002 per cent).
Substances Not Precipitated by Hydrogen Sulfide—Not more than 0.050 per cent as sulfates.
Iron (Fe)—Not more than 0.003 per cent.
Other Metals (as lead)—Not more than 0.02 per cent.

TESTS

Solution—Heat 5 grams to 40° C. in a mixture of 5 cc. of water and 5 cc. of hydrochloric acid. The salt should dissolve completely.

Sulfate—Dissolve 5 grams in 5 cc. of hydrochloric acid, dilute the solution to 50 cc., heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. No precipitate should be formed.

Arsenic—Dissolve 5 grams in 10 cc. of hydrochloric acid, bring to a boil, and allow to stand for 1 hour. The solution should be no more colored than a freshly prepared solution of 5 grams in 10 cc. of hydrochloric acid.

Substances Not Precipitated by Hydrogen Sulfide—Dissolve 4 grams in 10 cc. of hydrochloric acid, dilute to 200 cc., and precipitate the tin with hydrogen sulfide. Filter and evaporate 100 cc. of the filtrate to a few cubic centimeters, add a few drops of sulfuric acid, evaporate to dryness, ignite gently, and weigh. The weight of the residue should not exceed 0.0010 gram.

Iron—Warm the residue obtained in the previous test with 1 cc. of hydrochloric acid and a small crystal of potassium chlorate till chlorine is no longer evolved. Dilute with 20 cc. of water, add 2 cc. of hydrochloric acid and 1 cc. of 10 per cent ammonium thiocyanate solution. The red color should not be greater than is produced by 0.06 mg. of iron under the same conditions.

Other Metals (as lead)—Dissolve 1 gram in a mixture of 2 cc. of hydrochloric acid and 3 cc. of nitric acid. Boil till solution is complete and brown fumes are no longer given off in abundance. Cool, dilute to 10 cc., take 5 cc., and add 10 per cent sodium hydroxide solution till the precipitate first formed is redissolved. Cool, dilute to 40 cc., and add 10 cc. of hydrogen sulfide water. Any brown color should not be greater than is produced by 0.10 mg. of lead in 40 cc. of an alkaline solution to which 10 cc. of hydrogen sulfide water are added.

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Correction for Published Specification[1]

SODIUM BISMUTHATE

Assay—Not less than 75 per cent $NaBiO_3$.

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[1] THIS JOURNAL, **19**, 649 (1927).

Agreement on Shellac Label

The word "shellac" shall not be used by itself as a designation for material containing less than 100 per cent shellac gum cut in alcohol, the Federal Trade Commission stated in announcing settlement by stipulation of cases against three chemical firms. If the gum is contained in the material, but in quantities less than 100 per cent cut in alcohol, the designation "shellac compound" must be used.

BOOK REVIEWS

Chemistry. By W. H. Barrett. 151 pages. Oxford University Press, American Branch, New York, 1927. Price, $1.75.

This little volume is an introduction to the study of chemistry with special emphasis on practical applications and industrial processes.

The author takes up in order the various fundamental principles of the science of chemistry, and gives illustrations or description of experiments demonstrating these principles. He has very aptly woven in the historic developments of many of these fundamental theories and also gives the latest conception of these theories and phenomena.

A considerable number of our important industrial processes—such as the production of lime, cement, and mortar, fixation of nitrogen, the production of nitric and sulfuric acids, chlorine, and alkalies—are described where they seem to fit in with the description of theory.

The interesting natural cycles, such as carbon in its migration from fuels into the air as carbon dioxide and then through the plant structure to food for man and animal, is traced—also the nitrogen cycle. Isotopes and the structure of crystals and constitution of molecules and atoms are also discussed.

The author has not given many chemical formulas or equations, but such as he has used he has very clearly explained. The volume is very readable and admirably adapted as an introduction to the study of chemistry. It would serve well as supplementary reading in connection with an introductory course in this subject, whether in high school or college, to arouse an interest in this most vital and fundamental of our sciences.

Few errors have been noted in the volume. The technical processes are in general correctly described. The typographical work is excellent, illustrations being admirably reproduced.

J. C. Olsen

Titanium. With Special Reference to the Analysis of Titaniferous Substances. By William M. Thornton, Jr. A. C. S. Monograph Series, No. 33. 262 pages. 26 figures. The Chemical Catalog Company, Inc., 1927. Price, $5.00.

We cannot all know the authors of monographs, but if we could reviews would be very much less necessary, for from our knowledge of the author we could tell his capability of writing a book worthy of the appellation and of membership in the fine brotherhood of monographs published under the American Chemical Society. By those who know Doctor Thornton, his long familiarity with the chemistry of titanium, his painstaking methodical manner of work, and his meticulous exactness, it could only be accepted that his book would be worth while, and the book is good.

Beginning work twenty or more years ago on the chemistry of titanium minerals with Thomas L. Watson, who as state geologist of Virginia studied and wrote extensively on the peculiarly titaniferous series of rocks in the state, Doctor Thornton has had opportunities enjoyed by very few to "soak up" information on the little-known metal.

At the beginning of the century titanium was considered a rare element, but Clark showed that, far from being rare, it is one of the most plentiful, only eight being more abundant in the exposed rocks of the globe. With the realization of the plentitude of titanium, constant efforts have been made to make it play a useful part. At first most efforts were directed to its utilization in steel, but although still used, it does not form a component of the steel but merely acts as a cleanser. Lately the metal as found in the mineral ilmenite has taken on a totally new importance—the black mineral is being transformed to the whitest of pigments, with covering power and endurance beyond all other white pigments, and a promise that the hitherto almost worthless mineral will replace many thousand tons of salts of the more valuable lead and zinc, leaving them for the many uses where some commoner, cheaper substance is not "just as good."

Two companies were successfully making titanium-white pigments at the time the book went to press. Now the first, the Titan Co. A/S, of Norway, has been absorbed by the second, the Titanium Pigment Co., Inc. (a subsidiary of the National Lead Company), of Niagara Falls, N. Y. The processes of both are described. Since then other companies, here and abroad, have begun manufacture in line with the author's forecast. The use, manufacture, and analysis of ferrotitanium and more or less experimental alloys; titanium dyes, mordants, and strippers; the use of titanium in ceramics, smoke screens, arc light electrodes, Eckel's titan cement, and sundry other uses are described.

The larger part of the book, as befits such a publication, is given over to the chemistry of titanium, beginning with tests for its detection, giving methods of separation of titanium from other elements, oxidimetric methods, methods of analysis of titaniferous materials, including the author's own methods for rutile and ilmenite, followed by a chapter on the preparation of reagents, and finally by 27 pages of notes and references. These show something of the amount of labor put on the book; but to the reviewer's idea bibliographies at the end of a book are an abomination. A reference is a tool and, if in the form of a footnote, is a tool at hand—at the end of a chapter or a book it is a tool in the next room or down the hall.

Frank L. Hess

Hydrochloric Acid and Sodium Sulfate. By N. A. Laury. A. C. S. Monograph Series, No. 36. 127 pages. The Chemical Catalog Company, Inc., New York, 1927. Price, $4.00.

Mr. Laury has succeeded in thoroughly covering his subject with no waste of words. The short time required to read the book will be well spent regardless of whether the reader's interest is practical or academic.

Chapter II will prove a boon to the engineer, as it concentrates a large amount of physical and chemical data heretofore scattered through the literature. It is unfortunate that many of these data are tabulated; if they were plotted many future repeated interpolations would be avoided.

All standard methods of analysis of raw materials and finished product are given in detail, together with the usual specifications under which they are bought and sold. The description of various forms of furnaces is excellent and comparisons of usefulness extremely fair. The chapter on absorption covers the best modern practice very well. Containers and handling are treated in the same business-like way in the final chapter.

Realizing that this book is very much up to date, one cannot help feeling that the possibilities of improving the industry have been rather neglected in the past. It is hoped that the stimulus provided by Mr. Laury will end this period of neglect.

There are several errors in the book, although fortunately they are of such character as to be immaterial to the casual reader and so obvious to the practical man that he will not be misled by them.

W. S. Wilson

Acetate Silk and Its Dyes. By Charles E. Mullin. With a Foreword by Louis A. Olney. 473 pages. D. Van Nostrand Company, New York, 1927. Price, $6.00.

This book is a welcome addition to the sparse literature dealing with the problems confronting the dyer of the various rayons. The author has compiled in a creditable way his investigations and the work of other investigators on the processing and dyeing of cellulose acetate rayon. Since the dyeing of cellulose acetate rayon is radically different than the older viscose, nitrocellulose, and cuprammonium rayons, technical information for the dyeing of this new fiber is of unusual interest at this time.

The several kinds of cellulose acetate rayon are reviewed and their properties are described. The desizing, scouring, and bleaching of cellulose acetate rayon are considered briefly.

One of the author's chief aims has been to present a rather comprehensive survey of the new dyes which have recently been developed, especially for cellulose acetate rayon. In addition, he has described the methods for the application of these dyestuffs. The chapters on the dyeing of union materials containing cellulose acetate and other fibers will furnish valuable information to those dyers who are engaged in developing the unusual color effects which are possible when cellulose acetate is knitted into the same fabric with the other rayons, cotton, wool, and real silk. No book on dyeing is complete without colors. While the author has made no attempt to present a simple handbook for the average dyer, he could have widened the scope of usefulness of his book by showing the dyeings and especially the cross-dyeing effects obtainable by incorporating cellulose acetate with other fibers.

A desirable feature of the book is the systematic numbering of the different dyeing methods and the lists of dyestuffs which may be used to obtain certain solid- or cross-dyeing effects. Ample literature and patent references are given.

Joseph B. Quig

Essays on the Art and Principles of Chemistry. Including the First Messel Memorial Lecture. By Henry E. Armstrong. 276 pages. The Macmillan Co., New York, 1927. Price, $4.50.

If one will read the introduction to this book he will understand its preparation. Indeed, in a prefatory note the author gives as its purpose, "to emphasize the need to make our practice in chemistry scientific, etc." Then are recited the author's experiences in telling the story of chemistry in the several editions of the Encyclopedia Britannica, beginning with the ninth edition (1876). This was when

> Chemistry was still a laboratory subject—students were trained to use their hands and to be exact workers. * * * The would-be chemist can only learn to be a chemist by handling materials and lovingly studying their characteristics. * * * Chemistry is not the dull set of mere facts and formulae ill set out in the text-books—which with few exceptions are soulless: it is a living subject.

And in the setting forth of the author's contribution to the tenth edition (1902) of the Encyclopedia he offers his own views on a variety of subjects. In discussing molecular weight he remarks that this is a clear concept "not yet fully grasped by the physicist, who makes no proper distinction between the molecule (the acting dynamic unit) and the atom (the elementary unit)." And it is in this fashion that the author discusses his remaining Encyclopedia articles, which form the major portion of his present volume, and concludes with—

> I am seeking a hearing for interpretations which were advanced before Arrhenius was recognized, developed without the slightest knowledge of his speculations, brought before the Chemical Society and the British Association in 1885, the Royal Society in 1886 and often amplified in the interval. * * * My desire is to see chemistry made a rational study and an intellectual discipline—not a mere catalogue of facts and formulae, nor the subject of spurious mathematical deduction. * * * Chemical theory, today, is in a most destitute condition, a disgrace to our cloth * * * far too many chemists are working in alleys and backwaters without proper guidance or the possibility of appealing to reason.

The author of the present volume is an experienced and honored teacher, who has made splendid and lasting contributions to education in general, and while many of his criticisms may provoke resentment in us, at least as far as concerns his mode of presentment, his book deserves quiet, earnest, and thoughtful study from every lover of the science of chemistry.

Edgar Fahs Smith

Atomic Theory. An Elementary Exposition. By Arthur Haas. Translated by T. V. Verschoyle. 221 pages, 56 figures. D. Van Nostrand Company, Inc., New York, 1927. Price, $3.50.

There has been a flood of books lately claiming to give elementary exposition of modern atomic theory. Doctor Haas's book is an exception, in that it neither talks in terms of the kindergarten nor does it try to introduce an artificial element of interest beyond the inherent interest of the subject. It is not a book which a grammar-school pupil can read with profit. It is intended for college seniors and those who are just beginning graduate work. Although the author has not attempted to eliminate mathematics, he has introduced only enough mathematics to make his subject quantitatively understandable. The result is a book which will be useful to both the physicist and chemist. The book fills the need for a treatment simpler than that of Sommerfeld but more complete than the diluted sort of treatment given by the average "popular" exposition.

There are five chapters, dealing, respectively, with elementary quanta, theory of the hydrogen atom, x-rays, theory of the elements, and general theory of spectra and of atomic spectra. These five chapters are followed by a very useful ten-page summary, a synopsis of the symbols used in the book, a table of the universal constants of atomic physics, a historic summary of atomic theory up to 1924, and the usual name and subject indexes.

The book should be in every physics and chemistry library and it will be to the advantage of most seniors and graduate students in physics, physical chemistry, and chemistry to own a copy.

Wheeler P. Davey

Standards and Tests for Reagent and C. P. Chemicals. By Benjamin L. Murray. 2nd edition, revised and enlarged. xiii + 560 pages. D. Van Nostrand Company, Inc., New York, 1927. Price, $5.00.

The standards and tests for reagents given in the first edition [reviewed in This Journal, 12, 1035 (1920)] are reprinted almost without change, as indicated in the preface. "The changes made on reagent chemicals have resulted mainly from contact with users of the book, the criticisms of chemists in various laboratories where the text is regularly employed having been sought. The modifications here referred to are not large in number." The modifications consist of corrections of misprints in the first edition, slight changes in a few standards and tests, and inclusion of numerical limits for some reagents for which only general statements of requirements were given before.

For about 120 of the reagent chemicals the new edition gives also standards and tests for the c. p. grade. Many of the tests are the same as for the reagent grade but are made less severe by using smaller samples. Some tests and limits are identical for the two grades. Failure to respond to a test is commonly noted as representing a limit of 0.0000 per cent in the reagent grade and 0.000 per cent in the c. p. grade.

Standards and tests are given for the c. p. grade only of about 90 chemicals not listed in the first edition.

W. D. Collins

Soil Management. By Firman E. Bear. 2nd edition. 412 pages, 58 illustrations. John Wiley & Sons, Inc., New York; Chapman and Hall, Ltd., London, 1927. Price, $3.50.

Those teachers and students who found the first edition of this book helpful and instructive will be more than delighted with this new edition, since its scope of usefulness has been even further extended. It has been practically rewritten and much enlarged; the number of collateral reading references has been greatly extended, and the index improved.

While the chapter headings, and in fact the general treatment in the book, have remained much the same as in the earlier edition, the details of the subject matter are much more exhaustive and complete and many new pieces of research work are included. The chapters on fertilizers are especially up to date and have been brought in harmony with the newer movements in this rapidly developing industry. Doctor Bear's extended experience in this line will be especially valuable to the student of modern agriculture.

Like the earlier edition, the book is intended primarily for practical students of agriculture who have a knowledge of the sciences of chemistry, physics, geology, and botany, but anyone familiar with the vocabulary of these sciences will find it a useful guide in the consideration of many farm problems.

Oswald Schreiner

Modern Soap and Glycerin Manufacture. By E. T. Webb. 224 pages. Davis Brothers, London, 1927. Price, 25 s. net.

The book succeeds admirably in its aim to be a practical rather than an encyclopedic treatise on soap and glycerol production. The American reader will recognize the methods described as workable, although by no means the same in detail as those with which he is familiar in this country. In some respects either the English or the American procedure may suffer from a comparison of one with the other, but the fundamentals of soap boiling itself are essentially similar in the two countries in spite of striking differences in terminology, equipment, and details of processing.

The merit of the book is not limited to its wealth of practical detail; a comprehensive view of the subject is also presented. Figures IX and XIII, flow sheets for the production of 100 tons of pure soap and for the distillation of 100 tons of crude glycerol, respectively, are especially well conceived. Some rather positive opinions on disputed points are given, but these are the almost inevitable result of any one man's effort to write a practical guide book.

The chemistry of the book is very, very bad. The soap-making properties of hardened whale oil are discussed without recognition of the dependence of those properties upon the degree of hydrogenation. "Neutral silicate of soda" is mentioned without a clue as to what composition is meant and the discussion indicates a fundamental failure to understand the chemical behavior of sodium silicate. The false doctrine is preached that a soap cannot become rancid if all the fat is completely saponified. Even worse examples of chemical thought might be cited. The author's method of forecasting the solubility of a soap, if applied under American conditions, would sometimes be equivalent to a throw of the dice. Fortunately, the chemistry of the book is incidental.

A. S. Richardson

Die Katalyse in der organischen Chemie. By Paul Sabatier. Translated by Berthold Finkelstein, with the addition of a review of the literature from 1920 to 1926 by Hans Häuber. xi + 466 pages. 15 × 23 cm. Akademische Verlagsgesellschaft, m. b. H., Leipzig, 1927.

Sabatier's classic is here presented in German. The well-known original is a wonderful storehouse of experimental facts of catalysis with a minimum of theory. Sabatier has been the leading investigator in catalysis and a large portion of the observations are from his own laboratory. He has done an important service in bringing together and classifying so much information.

The body of this volume is an excellent translation of the second French edition. As the activity in this field has been intense much has been published since 1920. This new material has been well handled by Doctor Häuber, who has collected and classified the articles and patents that have appeared since 1920. A brief summary of each article is given with the reference. This section occupies 143 pages and is the most valuable part of the volume to American readers, as the book is already in English. A subject index, which covers the 1920–1926 literature references as well as the text, adds much to the value of the volume. Sabatier's numerous references have been touched up, but errors of volume and page numbers have not been corrected as they were in the English translation.

E. Emmet Reid

Führer durch die Chemische Literatur für Wissenschaft und Praxis. By Hans Bolte. 158 pages. L. Friedrichsen & Co., Hamburg, 1927. Price, 3.50 marks.

This little volume presents a handy reference list of the most important German chemical and chemico-technological books and periodicals published during the fifteen years ended January 1, 1927. An appendix includes similar works which have appeared since that date and up to March 15.

The aim is to provide the specialist with an efficient means of surveying the most valuable and the most up-to-date chemical literature of Germany and of orienting himself with respect to fields of specialization other than his own. To this end the works are classified under the main headings of "Theoretical Chemistry" and "Technical Chemistry," with subdivisions appropriate to the subject matter of each. In addition, the usual catalog data are supplemented by brief remarks as to the content of the book and for what and whom written. An attempt has been made to select the best works rather than to make the list absolutely complete. However, there is no effort at relative evaluation. The catalog is completed by subject and author indexes.

The American chemist should find this guide of great value in facilitating reference to recent works published in Germany. Hitherto no such list, compiled under one cover, has been available.

Paul R. Dawson

Diazotieren. By Siegfried Edlbacher. **Aetzalkalischmelze; Nitrieren.** By Ernst Maschmann. Lieferung 234; Abt. I, Chemische Methoden, Teil 2, Erste Hälfte, Heft 2 of Abderhalden's **Handbuch der biologischen Arbeitsmethoden.** 185 pages. Urban & Schwarzenberg, Berlin, 1927. Price, 10 marks.

The section on diazotization is only 5 pages long. Under the heading of aromatic diazo compounds brief discussions are given of the use of sodium, barium, and amyl nitrites. The diazotization of heterocyclic amines, such as pyrazolones, indoles, pyrroles, and purines, is merely mentioned in passing. Of the aliphatic diazo compounds, the preparation of diazoacetic acid ethyl ester by the method of Curtius is described, and that of diazomethane by the method of Staudinger and Kupfer.

More satisfactory from the standpoint of usefulness and instructiveness are the sections on alkali fusions and nitration. The first describes the methods of making fusions, the differences in behavior of sodium and potassium hydroxides, the use of aqueous and alcoholic solutions, and the oxidative and reductive processes in the fusions. Of interest to the biological chemist are the applications of the process to products such as proteins, blood pigment, adrenaline, thyroxin, plant pigments, tannins, resins, lignin, alkaloids, and saponins. Nor are the more usual applications in the organic laboratory neglected. These are illustrated by a wide variety of examples, some of them from recent publications.

"Nitration" is a monograph of 128 pages setting forth in considerable detail the general aspects of the subject, and giving a number of special applications. A large part of the work deals with the substitution of the nitro group for hydrogen. More briefly discussed are: the introduction of the nitro group by addition, by displacement of halogen, amino, carboxyl, and sulfonic acid.

Numerous recent references bring the work up to date. The presentation and array of material should prove of interest and value to the organic chemist.

Barnett Cohen

Chemie, Technologie und Analyse der Naphthensäuren. M. Naphtali. Volume III of a series of monographs entitled **Monographien aus dem Gebiete der Fett-Chemie,** edited by R. H. Bauer. 144 pages. Wissenschaftliche Verlagsgesellschaft, m. b. H., Stuttgart, 1927. Price, bound, 14 marks.

In this book the subject of naphthenic acids is discussed briefly under the following subdivisions or chapters: (1) introduction, giving a short account of the origin and history of naphthenic acids and their occurrence in petroleum; (2) separation and purification of the different acids from the crude naphthenic acid fractions from different sources; (3) the chemical and physical properties of the acids thus far identified and a short account of their physiological action; (4) the structure of the naphthenic acids which were first identified; (5) determination of constitution; (6) methods utilized for analysis of the crude acid mixtures; and (7) the technology of the naphthenic acids and of closely related organic compounds. The monograph will serve as a valuable aid for the organic chemist who is confused by the chaotic state in which we find petroleum chemistry at the present time. It is a valuable addition to the literature of petroleum, and the researches of such pioneer workers as Engler, Aschen, Gurwitsch, Cherchowsky, Budowski, Zelinsky, Zernick, and Holde are discussed in detail.

Treat B. Johnson

New Books

Aciers, Fers, Fontes. Tome II—Préparation, Haut Fourneau, Four à Puddler, Creuset, Four Martin, Convertisseur, Four Electrique. Alexis Jacquet. 2nd edition. 232 pp. Illustrated. Dunod, Paris. Price, 23 francs.

Determination of the Protein Requirements of Animals and of the Protein Values of Farm Feeds and Rations. H. H. Mitchell. Report of the Subcommittee on Animal Nutrition. *Bulletin* 55, National Research Council. 44 pp. National Research Council, Washington, D. C. Price, 75 cents.

Fabrication des Savons Industriels. Emulsions pour l'Ensimage et Huiles Solubles. R. Ehrsam. 3rd edition. 308 pp. Illustrated. Dunod, Paris. Price, 49 francs.

Fibres Textiles et la Teinture. Paul Bary. 256 pp. Illustrated. Dunod, Paris. Price, 58 francs.

Industrieofen in Einzeldarstellungen. Band II—Der Siemens-Martin-Ofen. Ernst Cotel. 150 pp. Otto Spamer, Leipzig. Price, 20 marks.

Laboratory Directions in Inorganic Chemistry. A. Silverman. 4th edition. 58 pp. D. Van Nostrand Co., New York.

Le Caoutchouc Durci. Encyclopédie du Caoutchouc et des Matières Plastiques. A. D. Luttringer. 198 pp. A.-D. Cillard, Paris. Price, 43 francs.

Molecular Spectra in Gases. Edwin C. Kemble, Raymond T. Birge, Walter F. Colby, F. Wheeler Loomis, and Leigh Page. *Bulletin* 57, National Research Council. 358 pp. National Research Council, Washington, D. C. Price, paper, $4.00; cloth, $4.50.

GOVERNMENT PUBLICATIONS

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.*

Bureau of Mines

Antimony in 1926. J. W. Furness. *Mineral Resources of the United States, 1926.* Part I, pp. 67–79. Paper, 5 cents.

Arsenic in 1926. V. C. Heikes. *Mineral Resources of the United States, 1926.* Part I, pp. 19–23. Paper, 5 cents.

Asphalt and Related Bitumens in 1926. G. R. Hopkins. *Mineral Resources of the United States, 1926.* Part II, pp. 51–69. Paper, 5 cents.

Barite and Barium Products in 1926. R. M. Santmyers and A. Stoll. *Mineral Resources of the United States, 1926.* Part II, pp. 81–89. Paper, 5 cents.

Comparison of Oils Derived from Coal and from Oil Shale. J. W. Horne and A. D. Bauer. *Reports of Investigations* 2832. 34 pp.

Feldspar in 1926. Jefferson Middleton. *Mineral Resources of the United States, 1926.* Part II, pp. 109–17. Paper, 5 cents.

Gold and Silver in 1925. General Report. J. P. Dunlop. *Mineral Resources of the United States, 1925.* Part I, pp. 731–68. Paper, 10 cents.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1925. Mine Report. C. W. Henderson. *Mineral Resources of the United States, 1925.* Part I, pp. 701–30. Paper, 5 cents.

Graphite in 1926. Jefferson Middleton. *Mineral Resources of the United States, 1926.* Part II, pp. 91–7. Paper, 5 cents.

Iron Ore, Pig Iron, and Steel in 1926. H. W. Davis. *Mineral Resources of the United States, 1926.* Part I, pp. 87–124. Paper, 10 cents.

Magnesium and Its Compounds in 1926. J. M. Hill. *Mineral Resources of the United States, 1926.* Part II, pp. 127–40. Paper, 5 cents.

Mercury in 1926 (Quicksilver). J. W. Furness. *Mineral Resources of the United States, 1926.* Part I, pp. 125–40. Paper, 5 cents.

Potash in 1926. A. T. Coons. *Mineral Resources of the United States, 1926.* Part II, pp. 119–25. Paper, 5 cents.

Railroad Fuel Oil Consumption in 1926. A. H. Redfield. *Circular* 6049. 6 pp.

Reduction of Breathing Losses from Vapor-Tight Lease Tanks. Ludwig Schmidt. *Reports of Investigations* 2834. 8 pp.

Salt, Bromine, and Calcium Chloride in 1926. A. T. Coons. *Mineral Resources of the United States, 1926.* Part II, pp. 71–80. Paper, 5 cents.

Sixteenth Semi-Annual Motor Gasoline Survey. E. C. Lane, D. J. Condit, and C. S. Luce. *Reports of Investigations* 2827. 2 pp.

Slate in 1926. A. T. Coons. *Mineral Resources of the United States, 1926.* Part II, pp. 99–107. Paper, 5 cents.

Some Methods of Producing Flowing Wells in the Salt Creek Field and Their Effect on Gas-Oil Ratios. K. B. Nowels. *Reports of Investigations* 2833. 50 pp.

Sources and Distribution of Major Petroleum Products, Atlantic Coast States—1926. E. B. Swanson. *Circular* 6050. 12 pp.

The Detection of Sulfur in Petroleum and Petroleum Distillates. F. W. Lane and John M. Devine. *Reports of Investigations* 2828. 7 pp.

The Function of Steam in the Limekiln. E. E. Berger. *Technical Paper* 415. 43 pp. Paper, 10 cents.

Tin in 1926. J. W. Furness. *Mineral Resources of the United States, 1926.* Part I, pp. 29–50. Paper, 5 cents.

United States Government Master Specifications for Lubricants and Liquid Fuels and Methods for Sampling and Testing. *Technical Paper* 323B. 121 pp. Paper, 15 cents.

Bureau of Standards

Alphabetical Index and Numerical List of United States Government Master Specifications, Promulgated by the Federal Specifications Board. (Complete to June 10, 1927.) *Circular* 319. 17 pp.

A Modified Method for Determination of the Copper Number of Paper. B. W. Scribner and W. R. Brode. *Technologic Paper* 354. 6 pp. Paper, 5 cents.

A Study of Problems Relating to the Maintenance of Interior Marble. D. W. Kessler. *Technologic Paper* 350. 91 pp. Paper, 35 cents.

Some Vulcanization Tests of Guayule Rubber. D. Spence and C. E. Boone. *Technologic Paper* 353. 8 pp. Paper, 5 cents.

United States Government Master Specification for Ink, Drawing, Black Waterproof. *Circular* 196. 4 pp. Paper, 5 cents.

Same. Leather, Bag. *Circular* 338. 6 pp. Paper, 5 cents.

Same. Leather, Hydraulic Packing (Vegetable Tanned). *Circular* 340. 6 pp. Paper, 5 cents.

Same. Paint, Olive Drab (Semipaste and Ready-Mixed). *Circular* 165. 12 pp. Paper, 5 cents.

Same. White, and Tinted Paints Made on a White Base, Semipaste and Ready-Mixed. *Circular* 89. 11 pp. Paper, 5 cents.

Bureau of the Census

Chemicals: Chemicals, Not Elsewhere Classified, Sulfuric, Nitric, and Mixed Acids, Rayon, and Salt. *Census of Manufactures, 1925.* 44 pp. Paper, 10 cents.

Manufactures of Nonferrous Metals and Alloys (except Precious Metals). *Census of Manufactures, 1925.* 23 pp. Paper, 5 cents.

Paints and Varnishes, Bone Black, Carbon Black, and Lampblack. *Census of Manufactures, 1925.* 21 pp. Paper, 5 cents.

Wood Distillation and Charcoal Manufacture. *Census of Manufactures, 1925.* 11 pp. Paper, 5 cents.

Chemical Warfare Service

Exhibit of the Chemical Warfare Service, United States Army. 15 pp.

Department of Agriculture

A Study of Lead Arsenate and Lime Spray Mixtures. P. A. Van Der Meulen and E. R. Van Leeuwen. *Journal of Agricultural Research,* 35 (August 15, 1927), 313–21.

Effect of Hydrogen-Ion Concentration on the Absorption of Phosphorus and Potassium by Wheat Seedlings. Jehiel Davidson. *Journal of Agricultural Research,* 35 (August 15, 1927), 335–46.

Forests and Water in the Light of Scientific Investigation. Raphael Zon. Reprinted with revised bibliography, 1927, from Appendix V of the Final Report of the National Waterways Commission, 1912. *Senate Document* 469, 62nd Congress, 2nd Session. 106 pp. Paper, 20 cents.

Tests of Methods for the Commercial Standardization of Raisins. E. M. Chace and C. G. Church. *Technical Bulletin* 1. 24 pp. Paper, 5 cents.

The Relation between the Vitamin B Content of the Feed Eaten and of the Milk Produced. S. I. Bechdel and H. E. Honeywell. *Journal of Agricultural Research,* 35 (August 1, 1927), 283–8.

The Use of the Electrolytic Bridge for Determining Soluble Salts. R. O. E. Davis. *Department Circular* 423. 14 pp. Paper, 5 cents.

Why Applications of Nitrogen to Land May Cause Either Increase or Decrease in the Protein Content of Wheat. W. F. Gericke. *Journal of Agricultural Research,* 35 (July 15, 1927), 133–9.

Department of Commerce

Sawdust and Wood Flour. Report of the National Committee on Wood Utilization. 26 pp. Paper, 10 cents.

Geological Survey

Quality of the Surface Waters of New Jersey. W. D. Collins and C. S. Howard. *Water-Supply Paper* 596-E. 31 pp.

Quicksilver Deposits of the Pilot Mountains, Mineral County, Nevada. W. F. Foshag. *Bulletin* 795-E. 11 pp. Paper, 5 cents.

Surface Water Supply of the United States, 1923. Part X—The Great Basin. N. C. Grover, A. B. Purton, H. D. McGlashan, F. F. Henshaw, C. G. Paulsen, and Robert Follansbee. *Water-Supply Paper* 570. 183 pp. Paper, 25 cents.

The Brown Iron Ores of West-Middle Tennessee. E. F. Burchard. *Bulletin* 795-D. 59 pp. Paper, 15 cents.

The Gillette Coal Field. Northeastern Wyoming. C. E. Dobbin and V. H. Barnett. With a Chapter on the Minturn District and the Northwestern Part of the Gillette Field. W. T. Thom, Jr. *Bulletin* 796-A. 64 pp. Paper, 35 cents.

Public Health Service

Report on Studies of the Efficiency of Water-Purification Processes. *Public Health Reports,* 42 (October 21, 1927), 2543–5.

Studies on Oxidation Reduction. IX—A Potentiometric and Spectrophotometric Study of Meriquinones of the *p*-Phenylene Diamine and the Benzidine Series. W. M. Clark, Barnett Cohen, and H. D. Gibbs. Supplement 54 to *Public Health Reports.* 61 pp. Paper, 10 cents.

Same. X—Reduction Potentials in Cell Suspensions. R. K. Cannan, Barnett Cohen, and W. M. Clark. Supplement 55 to *Public Health Reports,* 34 pp. Paper, 10 cents.

Treasury Department

Appendix to Regulations No. 3 (Formerly No. 61) Formulae for Completely and Specially Denatured Alcohol. Revised August, 1927. 14 pp.

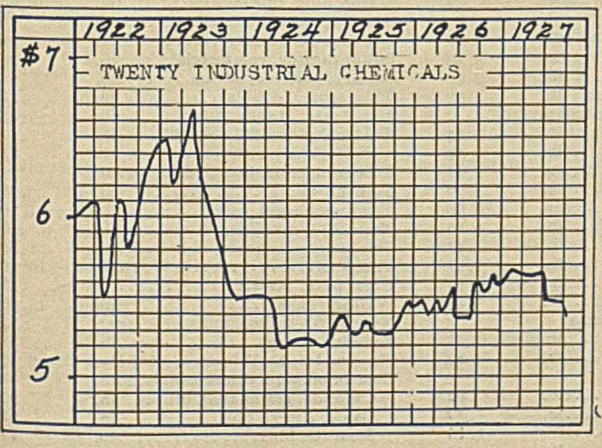
Regulations No. 2 (Being a Revision of Internal Revenue Regulations No. 60) Relating to Permits for the Manufacture of and Traffic in Intoxicating Liquors for Nonbeverage Purposes. Effective October 1, 1927. 285 pp.

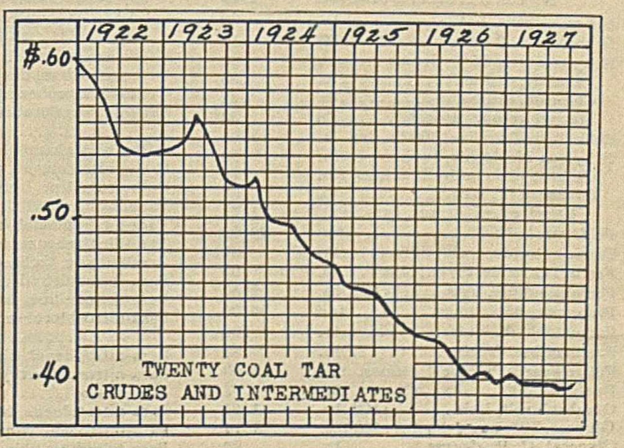
Regulations No. 3 (formerly No. 61) Relative to the Production, Tax Payment, etc., of Industrial Alcohol and to the Manufacture, Sale, and Use of Denatured Alcohol. Revised August, 1927. 146 pp. Paper, 20 cents.

MARKET REPORT—NOVEMBER, 1927

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON NOVEMBER 15

Acetanilide, tech., bbls	lb.	.21
Acetic anhydride, 92–95%, cbys	lb.	.29
Acetone, C. P., drums, wks	lb.	.12
Acetophenetidine, bbls	lb.	1.60
Acid, Acetic, 28%, c/1. bbls.	100 lbs.	3.38
56%, c/1. bbls	100 lbs.	6.34
Glacial, c/1. bbls	100 lbs.	11.92
Acetylsalicylic, bbls	lb.	.85
Anthranilic, 99–100%, drums	lb.	.98
Benzoic, tech., bbls	lb.	.58
Boric, bbls	lb.	.08½
Butyric, 60%, pure, 5-lb. bot	lb.	.55
Chloroacetic, mono-, bbls., wks	lb.	.25
Di-, cbys	lb.	1.00
Tri-, bbls	lb.	2.50
Chlorosulfonic, drums, wks	lb.	.15
Chromic, pure, 98%, drums	lb.	.37
Cinnamic, 5-lb. cans	lb.	3.25
Citric, U. S. P., kegs, bbls	lb.	.44
Cresylic, pale, drums	gal.	.70
Formic, 85%, cbys., N. Y.	lb.	.11
Gallic, U. S. P., bbls	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot	lb.	1.40
H, bbls., wks	lb.	.57
Hydriodic, 10%, U. S. P., 5-lb. bot	lb.	.65
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks	100 lbs.	1.05
Hydrofluoric, 30%, bbls., wks	lb.	.06
60%, bbls., wks	lb.	.13
Hydrofluosilicic, 35%, bbls., wks	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.36
Lactic, 22%, dark, bbls	lb.	.05½
66%, light, bbls., wks	lb.	.26
Mixed, tanks, wks	N unit	.06
	S unit	.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls	lb.	.55
Nitric, C. P., cbys	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks	lb.	.11
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys	lb.	.08
Picramic, bbls	lb.	.50
Picric, bbls. c/l	lb.	.30
Pyrogallic, tech., bbls	lb.	.86
Salicylic, tech., bbls	lb.	.37
Stearic, d. p., bbls. c/l	lb.	.11¼
Sulfanilic, 250-lb. bbls	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.35
66°, tanks, wks	ton	15.00
60°, tanks, wks	ton	10.50
Oleum, 20%, tanks, wks	ton	18.00
40%, tanks, wks	ton	42.00
Sulfurous, U. S. P., 6%, cbys	lb.	.05
Tannic, tech., bbls	lb.	.30
Tartaric, U. S. P., cryst., bbls	lb.	.35¾
Tungstic, kegs	lb.	1.00
Valeric, C. P., 10-lb. bot	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls	gal.	3.70
Amyl, 10%, Imp. drums	gal.	1.40
Butyl, drums, c/l. wks	lb.	.19¼
Cologne Spirit, bbls	gal.	3.90
Denatured, No. 5, Comp. denat. c/l, drs	gal.	.48
No. 1, Comp. denat., drs	gal.	.52
Isoamyl, drums	gal.	2.50
Isobutyl, ref., drums	lb.	...
Isopropyl, ref., drums	gal.	1.00
Propyl, ref., drums	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls	lb.	.65
Alpha-naphthylamine, bbls	lb.	.35
Alum, ammonia, lump, bbls., wks	100 lbs.	3.25
Chrome, casks, wks	100 lbs.	5.25
Potash, lump, bbls., wks	100 lbs.	3.10
Soda, bbls., wks	100 lbs.	3.25
Aluminum, metal, N. Y.	lb.	.26
Aluminum chloride, anhyd., drums	lb.	.35
Aluminum stearate, 100-lb. bbl.	lb.	.23
Aluminum sulfate, comm'l bags, wks	100 lbs.	1.40
Iron-free, bags, wks	100 lbs.	1.75
Aminoazobenzene, 110-lb. kgs	lb.	1.15
Ammonia, anhydrous, cyl., wks	lb.	.11
Ammonia water, 26°, drums, wks	lb.	.03
Ammonium acetate, kegs	lb.	.34
Bifluoride, bbls	lb.	.21
Bromide, 50-lb. boxes	lb.	.48
Carbonate, tech., casks	lb.	.08¾
Chloride, gray, bbls	100 lbs.	5.25
Lump, casks	lb.	.12
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls	lb.	.21
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.27½
Phosphate, dibasic, tech., bbls	lb.	.18
Sulfate, bulk, wks	100 lbs.	2.35
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums	gal.	1.90
Aniline oil, drums	lb.	.15¼
Anthracene, 80–85%, casks, wks	lb.	.60
Anthraquinone, subl., bbls	lb.	.90
Antimony, metal	lb.	.11¼
Antimony chloride, anhyd., drums	lb.	.17
Oxide, bbls	lb.	.16¼
Salt, Dom., bbls	lb.	.18
Sulfide, crimson, bbls	lb.	.25
Golden, bbls	lb.	.15
Vermilion, bbls	lb.	.37½
Tartrolactate, bbls	lb.	.45
Argols, red powder, bbls	lb.	.08
Arsenic, metal, kegs	lb.	.45
Red, kegs, cases	lb.	.10½
White, c/l. kegs	lb.	.04
Asbestine, bulk, c/l	ton	16.00
Barium carbonate, bbls., bags, wks	ton	47.50
Chloride, bags, wks	ton	57.50
Dioxide, bbls., wks	lb.	.13
Hydroxide, bbls	lb.	.04½
Nitrate, casks	lb.	.08
Barium sulfocyanate, 400-lb. bbls	lb.	.27
Barytes, floated, 350-lb. bbls., wks	ton	23.00
Benzaldehyde, tech., drums	lb.	.65
F. F. C., cbys	lb.	1.40
U. S. P., cbys	lb.	1.15
Benzene, pure, tanks, mills	gal.	.21
Benzidine base, bbls	lb.	.70
Benzoyl chloride, carboys	lb.	1.00
Benzyl acetate, cbys	lb.	1.30
Alcohol, 5-liter bot	lb.	1.40
Chloride, tech., drums	lb.	.25
Beta-naphthol, bbls	lb.	.24
Beta-naphthylamine, bbls	lb.	.63
Bismuth, metal, cases	lb.	2.25
Bismuth nitrate, 25-lb. jars	lb.	1.85
Oxychloride, boxes	lb.	3.10
Subnitrate, U. S. P., 25-lb. jars	lb.	2.20
Blanc fixe, dry, bbls	ton	80.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls	lb.	.08¼
Borax, powd., bbls	lb.	.04½
Bordeaux mixture, bbls	lb.	.11
British gum, com., c/l	100 lbs.	4.37
Bromine, bot	lb.	.47
Bromobenzene, drums	lb.	.50





Bromoform, 5-lb. bot..........lb.	1.65
Butyl acetate, 100-gal. drums...gal.	1.55
Cadmium bromide, 50-lb. jars....lb.	1.20
Cadmium, metal, boxes.........lb.	.70
Cadmium sulfide, cs............lb.	1.20
Caffeine, U. S. P., 5-lb. cans.....lb.	3.05
Calcium acetate, bags......100 lbs.	3.50
Arsenate, bbls................lb.	.07½
Carbide, drums...............lb.	.05½
Chloride, drums, wks.........ton	21.00
Cyanide, 100-lb. drum.........lb.	.30
Lactate, tech., bbls...........lb.	.35
Nitrate, bbls..................ton	52.00
Phosphate, monobas., bbls....lb.	.07
Tribas., bbls...............lb.	.11
Calcium carbonate, tech., bgs. 100 lbs.	1.00
U. S. P., precip., 175-lb. bbl....lb.	.06½
Camphor, Amer., bbls..........lb.	.62
Jap., cases....................lb.	.60
Camphor, monobrom, cs.........lb.	1.85
Caramel, bbls..................gal.	.63
Carbazole, bbls.................lb.	.15
Carbon, activated, drums......lb.	.05
Carbon bisulfide, drums........lb.	.05½
Carbon black, cases............lb.	.12
Carbon dioxide, liq., cyl........lb.	.06
Carbon tetrachloride, drums.....lb.	.07
Casein, stand. gr., bbls.........lb.	.18
Cellulose acetate, kegs..........lb.	1.40
Cerium oxalate, kegs............lb.	.32
Charcoal, willow, powd., bbls....lb.	.06
China clay, imp., bgs......100 lbs.	15.00
Chloral hydrate, drums..........lb.	.60
Chloramine U. S. P., 5-lb. bot...lb.	1.75
Chlorine, liq., c/l., cyl...........lb.	.04
Chlorobenzene, mono-, drums...lb.	.07
Chloroform, tech., drums.......lb.	.20
Chromium acetate, 20° sol., bbls. lb.	.05½
Coal tar, tanks, bbls., wks.....gal.	.07
Cobalt, metal, kegs.............lb.	2.50
Cobalt oxide, bbls...............lb.	2.00
Cod-liver oil, bbls.............bbl.	41.00
Collodion, drums................lb.	.23
Copperas, c/l., bulk...........ton	13.00
Copper, metal, elec.........100 lb.	12.90
Copper carbonate, bbls..........lb.	.16¼
Chloride, bbls.................lb.	.28
Cyanide, drums................lb.	.48
Oxide, red, bbls...............lb.	.16½
Sulfate, c/l., bbls.........100 lb.	5.00
Cotton, soluble, bbls...........lb.	.40
Cream tartar, bbls..............lb.	.26½
Cyanamide, bulk, N. Y. ....Ammon. unit	1.67½
Diaminophenol, kegs............lb.	3.80
Dianisidine, kegs...............lb.	3.25
Dibutyl phthalate, drums, wks..lb.	.29½
Diethylaniline, drums...........lb.	.55
Diethylene glycol, l. c. l. lots, drums.....................lb.	.20
Carload lots, drums.......lb.	.15
Diethylphthalate, drums........lb.	.24
Diethylsulfate, tech., drums.....lb.	.20
Dimethylaniline, drums.........lb.	.30
Dimethylsulfate, drums.........lb.	.45
Dinitrobenzene, drums..........lb.	.15½
Dinitrochlorobenzene, bbls......lb.	.15
Dinitronaphthalene, bbls........lb.	.32
Dinitrophenol, bbls.............lb.	.31
Diphenylamine, bbls............lb.	.45
Diphenylguanidine, bbls........lb.	.68
Epsom salt, tech., bbls., c/l., N. Y..................100 lbs.	1.10
Ether, nitrous, bot..............lb.	.90
Ether, U. S. P., drums..........lb.	.15
Ethyl acetate, 85%, drums.....gal.	.90
Bromide, drums...............lb.	.50
Chloride, drums...............lb.	.22
Methyl ketone, drums.........lb.	.30
Ethyl benzyl aniline, 300-lb. drs..lb.	1.05
Ethylene dichloride, tanks......lb.	.06
Chlorohydrin, anhyd., drums..lb.	.75
Glycol, c/l., wks..............lb.	.30
Ethyl ether, drums, cars..gal.	1.79
Feldspar, bulk..................ton	20.00
Ferric chloride, tech., bbls......lb.	.07½
Ferrous chloride, cryst., bbls.....lb.	.05
Ferrous sulfide, bbls........100 lbs.	2.50
Fluorspar, 95%, bags...........ton	25.00
Formaldehyde, bbls.............lb.	.09
Formaniline, drums.............lb.	.38
Fuller's earth, bags, c/l., mines..ton	15.00
Furfural, 500-lb. drs., c/l.......lb.	.17½
Glauber's salt, bbls.........100 lbs.	1.05
Glucose, 70°, bags, dry.....100 lbs.	3.14
Glycerol, C. P., drums..........lb.	.22
G salt, bbls.....................lb.	.50
Hexamethylenetetramine, tech., drums.....................lb.	.62
Hydrogen peroxide, 25 vol., bbls......................lb.	.06½
Hydroquinone, kegs............lb.	1.25
Indigo, 20%, paste, bbls........lb.	.14
Iodine, crude, 200-lb. kgs.......lb.	4.20
Iodine, resubl., jars............lb.	4.65
Iodoform, bot..................lb.	6.00
Iridium, metal.................oz.	110.00
Kieselguhr, bags...............ton	60.00
Lead, metal.............. 100 lb.	6.25
Lead acetate, bbls., white......lb.	.15
Arsenate, bbls...............lb.	.14
Oxide, litharge, bbls..........lb.	.08¾
Red, bbls.....................lb.	.09¾
Peroxide, drums..............lb.	.25
White, basic carb., bbls.......lb.	.09
Sulfate, bbls..................lb.	.08¼
Lime, hydrated, bbls.......100 lbs.	.85
Lime, live, chemical, bbls., wks. ....100 lbs.	1.05
Limestone, ground, bags, wks...ton	4.50
Lithium carbonate, 100-lb. kgs...lb.	1.45
Lithopone, bbls.................lb.	.06⅛
Magnesite, crude...............ton	36.00
Calcined, 500-lb. bbls., wks...ton	48.00
Magnesium, metal sticks, wks...lb.	.85
Magnesium carbonate, bags.....lb.	.06¾
Chloride, drums..............ton	37.00
Fluosilicate, cryst., bbls.......lb.	.10
Oxide, U. S. P., light, bbls....lb.	.42
Manganese chloride, casks......lb.	.08
Dioxide, 80%, bbls...........ton	80.00
Sulfate, casks.................lb.	.07
Mercury bichloride, cryst., 25 lbs. lb.	1.58
Mercury, flasks, 75 lbs.........flask	129.00
Meta-nitroaniline, bbls..........lb.	.72
Meta-phenylenediamine, bbls....lb.	.90
Meta-toluylenediamine, bbls....lb.	.72
Methanol, pure, tanks.........gal.	.50
Denaturing grade, tanks.....gal.	.75
Methyl acetone, drums........gal.	.88
Salicylate, cases.............lb.	.42
Methyl chloride, cylinders......lb.	.55
Michler's ketone, bbls..........lb.	3.00
Monoethylaniline, drums.......lb.	1.05
Naphtha, solvent, tanks.......gal.	.35
Naphthalene, flake, bbls........lb.	.05
Nickel, metal...................lb.	.35
Nickel salt, single, bbls........lb.	.10¼
Double, bbls..................lb.	.09
Niter cake, bulk...............ton	4.50
Nitrobenzene, drums...........lb.	.08½
Oil, castor, No. 1...............lb.	.13
China wood, bbls............lb.	.15¼
Coconut, Ceylon, tanks.......lb.	.08⅝
Cod, N. F., tanks...........gal.	.63
Corn, crude, tanks, mills.....lb.	.09¼
Cottonseed, crude, tanks......lb.	.09¼
Lard, edible, bbls............lb.	.16¾
Linseed, bbls.................lb.	.096
Menhaden, crude, tanks.....gal.	.46
Neat's-foot, pure, bbls........lb.	.18¼
Oleo, No. 1, bbls.............lb.	.18½
Olive oil, denat., bbls........gal.	1.60
Foots, bbls.................lb.	.09¾
Palm, Lagos, casks...........lb.	.08
Peanut, crude, tanks.........lb.	.12
Perilla, bbls..................lb.	.14
Rapeseed, bbls., English.....gal.	.88
Red, bbls.....................lb.	.09
Soy bean, crude, bbls.........lb.	.09¾
Sperm, 38°, bbls............gal.	.84
Whale, bbls., natural winter..gal.	.76
Ortho-aminophenol, kegs........lb.	2.20
Ortho-anisidine, drums.........lb.	2.35
Ortho-dichlorobenzene, drums...lb.	.06
Ortho-nitrochlorobenzene, drums ....lb.	.32
Ortho-nitrophenol, bbls.........lb.	.85
Ortho-nitrotoluene, drums......lb.	.17
Ortho-toluidine, bbls...........lb.	.29
Palladium, metal...............oz.	80.00
Para-aminophenol, kegs.........lb.	1.15
Para-dichlorbenzene............lb.	.17
Paraldehyde, tech., drums......lb.	.27
Para-formaldehyde, cases.......lb.	.45
Para-nitroaniline, drums........lb.	.48
Para-nitrochlorobenzene, drums ....lb.	.32
Para-nitrophenol, bbls..........lb.	.50
Para-nitrosodimethylaniline, bbls......................lb.	.92
Para-nitrotoluene, bbls.........lb.	.30
Para-phenylenediamine, bbls....lb.	1.15
Para-toluidine, bbls............lb.	.40
Paris Green, 500-lb. kgs.........lb.	.19
Phenol, drums..................lb.	.17
Phenolphthalein, drums.........lb.	1.30
Phenylethyl alcohol, 1-lb. bot....lb.	7.00
Phosphorus, red, cases..........lb.	.60
Phosphorus trichloride, cyl......lb.	.45
Phthalic anhydride, bbls........lb.	.18
Platinum, metal................oz.	95.00
Potash, caustic, drums..........lb.	.07⅛
Potassium acetate, kegs.........lb.	.29
Bicarbonate, casks............lb.	.09
Bichromate, casks............lb.	.08¼
Binoxalate, bbls..............lb.	.16
Bromate, cs...................lb.	.35
Carbonate, 80–85%, calc., casks......................lb.	.05⅝
Chlorate, kegs................lb.	.08½
Chloride.....................ton	34.55
Cyanide, cases................lb.	.55
Meta-bisulfite, bbls...........lb.	.11
Permanganate, drums.........lb.	.15¼
Prussiate, red, casks..........lb.	.39
Yellow, casks...............lb.	.18½
Titanium oxalate, bbls........lb.	.25
Pyridine, drums...............gal.	1.50
Quinine bisulfate, 100 oz........oz.	.40
Sulfate, 100-oz. cans..........oz.	.40
Resorcinol, tech., kegs..........lb.	1.30
Rochelle salt, bbls., U. S. P......lb.	.23
R salt, bbls....................lb.	.45
Saccharin, cans.................lb.	1.75
Salt cake, bulk.................ton	19.00
Saltpeter, gran., bbls...........lb.	.06
Silica, ref., bags...............ton	18.00
Silver nitrate, 16-oz. bot........oz.	.41⅛
Soda ash, 58%, light, bags, contract, wks............100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks.........100 lbs.	3.10
Sodium acetate, bbls............lb.	.04½
Benzoate, bbls................lb.	.50
Bicarbonate, bbls........100 lbs.	2.00
Bichromate, casks............lb.	.06¼
Bisulfite, bbls.................lb.	.04
Bromide, bbls.................lb.	.42
Carbonate, sal soda, bbls., 100 lbs.	1.30
Chlorate, kegs................lb.	.06¼
Chloride, bags...............ton	12.00
Cyanide, cases................lb.	.20
Fluoride, bbls.................lb.	.08¾
Metallic, drums, 12¼-lb. bricks, lb.	.27
Naphthionate, bbls...........lb.	.55
Nitrate, crude, bags, N. Y. ....100 lbs.	2.45
Nitrite, bbls..................lb.	.08½
Perborate, bbls...............lb.	.21
Peroxide, cases...............lb.	.27
Phosphate, trisod.............lb.	.04
Picramate, kegs...............lb.	.69
Prussiate, bbls................lb.	.12
Silicate, drums, tanks, 40°, 100 lbs.	.75
Silicofluoride, bbls............lb.	.04¾
Stannate, drums..............lb.	.48½
Sulfate, anhyd., bbls..........lb.	.02¼
Sulfide, cryst., bbls...........lb.	.02½
Solid, 60%.................lb.	.03½
Sulfocyanide, bbls............lb.	.40
Thiosulfate, reg., crys., bbls..lb.	.02½
Tungstate, kegs..............lb.	.85
Strontium carbonate, bbls......lb.	.08
Nitrate, bbls..................lb.	.08¾
Strychnine alkaloid, 100 oz., powd......................oz.	.56
Sulfate, powder..............oz.	.38
Sulfur, bulk, mines, wks........ton	19.00
Sulfur chloride, red, drums......lb.	.05½
Yellow, drums...............lb.	.03¾
Sulfur dioxide, commercial, cyl..lb.	.08½
Sulfuryl chloride, drums........lb.	.65
Thiocarbanilid, bbls............lb.	.22
Tin, Amer., stand..............lb.	.58
Tin bichloride, 50% sol., bbls....lb.	.17¾
Oxide, bbls...................lb.	.75
Titanium oxide, bbls., wks......lb.	.40
Toluene, tanks................gal.	.35
Tribromophenol, cases..........lb.	1.10
Triphenylguanidine, drums......lb.	.69
Triphenyl phosphate, bbls......lb.	.75
Tungsten................WO$_3$ unit	10.50
Urea, pure, cases...............lb.	.18
Whiting, bags..................ton	18.00
Xylene, 5°, drums, mills.......gal.	.35
Xylidine, drums................lb.	.37
Zinc, metal, N. Y......... 100 lbs.	6.40
Zinc ammonium chloride, bbls...lb.	.06¼
Chloride, granulated, drums...lb.	.06¼
Oxide, Amer., bbls...........lb.	.07½
Stearate, bbls................lb.	.19
Zinc dust, bbls., kegs, c/l.......lb.	.09