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## EDITORIALS

### The Washington Meeting

THE date of the Washington meeting of the AMERICAN CHEMICAL SOCIETY has been set for the week beginning Monday, April 21, 1924, with hotel headquarters at the New Willard. The local section has been fortunate in securing the Central High School, which is sufficiently large to accommodate all divisions and sections, as the meeting place.

Local sections which have long desired to have one of the semiannual meetings of the SOCIETY in their city, but have been deterred from extending an invitation largely because of the expense involved, will be sure to look with favor upon the innovation which the Washington Section has voted to attempt. The spring meeting will be financed wholly within the chemical profession. Industries and interested friends will not be solicited for contributions, but those attending the meeting will be offered entertainment which, it is thought, will be adequate, and the registration fee will be set at a figure to cover the expense involved. The members of the local section hope to demonstrate that a successful meeting of the SOCIETY can be held without great financial outlay on the part of the local section, and to establish a precedent for other sections to follow in entertaining the SOCIETY in future.

Another innovation will be that on the days following the general meeting and symposia on Tuesday the divisions and sections will meet in the mornings only, leaving the afternoon of each day for excursions, both scientific and popular, for small group meetings, and for relaxation from close attention upon scientific programs.

It is none too early to begin to plan to attend the Washington meeting. The time set for the convention is one of the most delightful seasons of the year, and Washington, always popular with sightseers, is unusually attractive at this particular season of the year. Washington has splendid hotel facilities, but they will be taxed to the utmost during the Easter holidays, and in order to secure the best and most satisfactory accommodations we urge members to make their hotel reservations now. If you desire, H. C. Fuller, chairman of the Committee on Hotels and Transportation, Institute of Industrial Research, Washington, D. C., will make reservations for you. In the near future the announcement of other committeemen will be made, in order that members may make all arrangements directly with the appropriate committees.

### Japan

WE DO not know as yet to what extent the chemists and the chemical industry of Japan may have suffered from the earthquake, flood, and fire, but we want our many readers in that country to know that their misfortune has been very much upon our minds and that we have hoped from day to day to receive more definite information. We have been unable to obtain word from our Japanese correspondent since the catastrophe, but hope that our failure to hear does not indicate disaster. Notwithstanding a number of natural handicaps, Japan has made great progress in the chemical industry and we sincerely trust that the gains made at such great cost of time and labor have not been wholly lost.

### Alcohol, the Chemical

JUST a year ago we made suggestions in an editorial looking to an improvement in the administration of the National Prohibition Act, so far as it concerns high-proof alcohol used for nonbeverage purposes. In the interim the Commissioner of Internal Revenue has taken a progressive step in organizing an Alcohol Trades Advisory Committee composed of men representing associations of alcohol-using industries, and the AMERICAN CHEMICAL SOCIETY has representation upon this committee. The appointment of the committee and the whole-hearted manner in which the Commissioner of Internal Revenue and the officials of the Prohibition Unit have sought the advice of the group are most encouraging. Officials who have been more concerned with the prohibitory than with the permissive phases of alcohol legislation are beginning to realize that there is such a thing as alcohol, the chemical, and that in prohibiting the use of intoxicating beverages it is necessary to do so without arresting the development of uses of alcohol, the chemical raw material.

A statement has recently been issued by the Alcohol Trades Advisory Committee outlining the present situation and including an appendix in which are listed about five pages of lawful uses of alcohol, pure and denatured, and a chart showing some of the many uses of ethyl alcohol. The distribution of this statement will, it is believed, do much to make available information which, while common knowledge to the scientist, is a revelation to the average Government official and law-maker. The statement contains the following recommendations:

I—As alcohol is admittedly a basic chemical essential to our national defense, industrial and economic development, and even to the advancement of civilization itself, all who believe in true law enforcement should recognize the insufferable situation to which chemical industry has been brought by failure heretofore properly to enforce the industrial alcohol features of the National Prohibition Act, and should make certain that it is administered as intended by Congress.

II—The Alcohol Trades Advisory Committee believes that the action of a former Commissioner of Internal Revenue in vesting in a Federal Prohibition Commissioner, not equipped with the essential technical and economic knowledge and training, the duties of carrying out the provisions of the National Prohibition Act, concerning the manufacture, transportation, sale, and use of industrial alcohol, was illegal by implication, illogical by any method of sound reasoning, economically impracticable, and should be forthwith corrected.

The Commissioner of Internal Revenue should designate a Deputy Commissioner of Internal Revenue, or appoint an Industrial Alcohol Commissioner, to take over the administration of that portion of the law relating to the manufacture, sale, and use of high-proof alcohol, pure and denatured for non-beverage uses. Collectors of Internal Revenue and Civil Service revenue officers should be selected to assist him, as is customary in the enforcement of other internal revenue statutes. It follows that such a Deputy or Industrial Alcohol Commissioner should possess suitable technical knowledge, training, and experience. It should be his duty to issue permits to manufacture, withdraw, and use industrial alcohol of any kind, a copy of each permit at the time of issuance to be delivered to the Prohibition Commissioner so that he might police operations. In this way, efficient and scientific administration would be assured and at the same time the Prohibition Commissioner would be relieved from routine work incidental to serving legitimate industry, and could devote the necessary time to his logical duty of enforcing the prohibitory features of the law. Furthermore, the two agencies, coördinating, would be a check upon each other. *It would not require any change whatsoever in the*

law, but merely a revision of Regulations 60 and 61, to carry this recommendation into effect.

III—If agreeable to the Commissioner of Internal Revenue, this Alcohol Trades Advisory Committee will act in an advisory capacity for the purpose of assisting such Deputy Commissioner of Internal Revenue or Industrial Alcohol Commissioner in investigating applications for permits and furthering the uses of alcohol in scientific research and lawful industry.

Secretaries of the local sections have been sent copies of the entire statement. This subject should be discussed before local sections and every effort made to have the public gain a better understanding of all that is involved in the use of alcohol for nonbeverage purposes.

## Standards and the Metric System

UNDER the progressive leadership of the Department of Commerce much has been accomplished in simplified practice and standardization with the task but just begun. Needless sizes and styles are being eliminated in various lines. Dimensions are being standardized and ultimately the benefit will be derived in the more efficient use of raw material and the lowering of costs, not only in manufacture, but in stocks and turnover.

This is all commendable and we have heartily supported the department's program. We sincerely hope that when this project has fully established itself with manufacturers, jobbers, dealers, and the public, a real simplification and standardization may take place by first abandoning the fallacy of whole numbers in dimensions, and then simplifying our systems of weights and measures. This inevitably means the adoption of the metric system. We do a great deal of thinking and hard work to gain an export market, and with the metric system obligatory in thirty-four countries and optional in eleven more, it is easy to see that, with the notable exception of Great Britain, real effort to do business abroad means the use of the metric system in catalogs, in packages, and in dimensions. Will the American manufacturer be content to carry packages in two systems upon his shelves? Can he afford to do so?

We are confident that much of our difficulty comes through the adhesion to whole numbers or major fractions in the dimensions of materials, with a consequent lack of efficiency. Is it not true that in the design of most manufactured articles a definite size is first chosen because it looks about right and then decided arbitrarily without respect to the size, thickness, or strength which it should have from the standpoint of utility and performance of a definite piece of work? Sometime dimensions will be determined with respect to satisfying rigid laboratory tests, just as materials are tested at present. Dimensions will then require expression in the convenient metric units and mechanics who now are indifferent to the metric system will insist upon its use.

Efficient standardization follows initial diversity for, from a variety, the survival of the fittest brings forth the designs best adapted to service. Automobile experience is an example. From the great variety of cars designed we find some disappearing because they are unsatisfactory, others finding their special place and developing it, and still others produced in quantity and becoming standard because of the service they perform. The standards of today, therefore, may not be expected to serve as the standards for tomorrow, and with the oncoming generation learning to use the metric system in the radio, in the laboratory, and in other directions, may we not soon base our simplified practice and our standardization upon the only system that is international in the broadest sense, cast aside confusion due to the many systems we now endeavor to handle, and concentrate upon the education of the people at large to the appreciation and use of metric units?

## Recognition of Scientists

L. H. BAEKELAND, just returned from an extensive trip with renewed appreciation for the opportunities and privileges of the United States, recently brought to our attention the desirability of having Congress recognize in some specific and definite way the triumphs of our men of science, particularly those in department circles. Then in the editorial section of the *New York World* for September 2, Ellwood Hendrick discussed the same sentiments and made a plea for such recognition by Congress. We wish to add our voice and urge that something be done in a proper way to have our law-makers realize that "the United States is the only civilized country in the world that does not recognize distinguished service by civilians. In the British Empire they make them lords or knights—and we cannot do that. In France, Italy, Spain, Belgium, Portugal, China, Japan, and even in Soviet Russia, they give decorations. We do not give decorations to civilians. Moreover, the insignia of decorations have been preempted by so many private organizations in this country that a button in the lapel of a man's coat is without its significance elsewhere."

But there are other ways in which this Nation can express its thanks. Perhaps some day we may go as far as our neighbor Canada and grant a substantial annuity to a man who has made a scientific discovery of great importance to the public. There seems no reason why Congress could not pass an act, engrossed and signed by the President of the United States, consisting of a proper preamble and resolution commending and expressing gratitude to a man who has devoted many years of his life, his ability as a scientist and perhaps as an inventor, to the welfare of the republic.

Such a document would be invaluable to the recipient. Moreover, the adoption of a policy of this kind might be the first step in working out a really adequate plan for rewarding scientists, many of whom have steadfastly refused more remunerative offers out of pure patriotism. Such action might be taken only upon the retirement of a departmental head or bureau chief, but those are details. The point we want to make now is that the devotion and sacrifice of our chemists to the science should be recognized in some way.

## Electrical Wars

THE efforts of some misinformed enthusiasts to discredit chemical warfare have been of small avail, thanks to the readiness with which the American people have grasped the truth. Perhaps those who oppose the application of the science, chemistry, to defense would also limit research in electricity because of the prediction made by Professor Low of London. He suggests the possibility of using jets of electrically charged water to kill horses and men; calls attention to the efficiency of wireless control of tanks and airplanes; of wireless telephony, sight, heat, and power; of battleplane engines developing wireless power to destroy aircraft within a wide radius; of the possibility of conducting propaganda striking terror into the home by means of wireless receivers; of airplanes with electric impulse by which guns could be fired at an enormous rate; of electrically controlled rockets operated on wires for wrecking planes; and, of course, the wireless-controlled torpedo with a wireless sighted periscope controlled by a secret combination of wave lengths. Perhaps we may have controllable lightning and monsters of the air and sea, the progenitors of which are already an actuality.

However much we should like to see the coming of the millennium, there is so far nothing to justify relaxation in research in any of the sciences, and least of all in chemistry.

## Institute of American Meat Packers

AMONG the associations of industrialists engaged in scientific research, none deserves more encouragement than the Institute of American Meat Packers. Making progress cautiously, the institute has nevertheless accomplished much through its Committee on Scientific Research, and the vista of the future is most encouraging.

Arthur Lowenstein, vice president of Wilson & Company, has established a substantial fellowship on the prevention of meat spoilage, and the institute has sanctioned a research fellowship at Mellon Institute on the utilization of by-products. A series of lectures under the joint auspices of the School of Commerce and Administration of the University of Chicago and the institute has been inaugurated, and courses of instruction have been arranged so that the employees in the packing plants will have a better opportunity to fit themselves for their work. The courses are intended primarily for those now occupying minor executive positions and who are ambitious to become executives. Both day courses for full-time study and evening courses are announced. This experiment will be watched with great interest. Correspondence work will begin later in the academic year and research to extend the boundaries of scientific knowledge will be undertaken soon.

Concurrently, the Committee on Scientific Research of the institute is developing plans for extensive work under the direction of its own staff, and has in view such important investigations as a study of a substitute for sugar in meat curing. Coöperation is being sought with trade organizations, Government bureaus, and others having a mutual interest in the problems of the packing industry, and following a scientific survey of the industry we may expect an announcement of an extensive and detailed program.

The packing industry has always been known for its achievements in applied science and the prosecution of fundamental research. This work has been done in the individual plants and laboratories. The coöperative research of the institute can be carried to success without detracting from the importance of these individual laboratories. There are sufficient fundamental problems to engage the thought and energy of all concerned.

## Trade Secrecy

A PRESS dispatch dated London, October 17, states:

A secret formula for making dye by a method said to require only a fraction of the usual cost has been carried to the grave by a London pauper, Robert Culver, who learned from a German relative years ago and brought it to England, where he organized a dye manufacturing company.

The concern, however, failed through dishonesty of some of its officials and Culver was reduced to poverty. He died recently in a poorhouse without telling any one of the process.

We know nothing of the value of the secret in question, but we desire to emphasize again that secrecy in industrial processes and in scientific work belongs in the past and has little part in modern affairs. There are still those who jealously guard all the minute details of any formula or process, but they are outnumbered by those who know that in skill and technic there lies the protection which justifies them in discussing in some detail the various steps in a particular formula. As one such expressed himself, "My formula is as open as a violin. There it is. Now play it." Our own experience with certain much-discussed formulas and patents indicates that those with training and a deep interest can learn to play and that in a frank discussion of processes those who give always profit directly by the exchange of ideas.

## Making the Chemical Show Chemical

CRITICISM of the Ninth National Exposition of Chemical Industries has taken much the same form and come from much the same sources as that of its predecessors—"Chemical industries were sadly lacking although everyone with something to sell that industry was represented. The show has become more and more an equipment show and not a chemical one." This type of criticism may be justified, but hardly can it be when unaccompanied by suggestions of ways and means to overcome the trouble.

Let us look for a moment at the reasons for the absence of strictly chemical manufacturers from such a gathering. The most natural and perhaps the most important reason for this apparent defection of the key section of the exposition has been that chemical manufacturers have failed to get monetary returns for their expenditures on exhibits. Quite naturally altruism is no more a part of the scheme of the chemical manufacturer than it is of any other, so that it is necessary to take this point into serious consideration. The equipment manufacturers have found the exposition profitable and hence have continued to exhibit. They have taken advantage of one very definite point in preparing their exhibits which the chemical group apparently failed to consider. *New* equipment and *new* wrinkles in old equipment are shown alongside the same old bottles, kegs, and barrels of chemicals which present nothing in the least new. In this lies the secret of the success of the one and the failure of the other.

Visitors to recent shows will recall the long decorative hangings of crystals of copper sulfate in the booth of one chemical manufacturer, for example, which were truly beautiful. But what did they mean to the chemical consumer? Nothing! He was not interested in the least in buying copper sulfate for decorating either his home or his plant. He was interested, let us say, in its use in preparing a new insecticide, but he was shown a decoration. The attention value of such decorations in coaxing visitors to pass near a booth is great, but their value in getting visitors into the booth to buy is an altogether different matter. To continue the case, let us suppose that within the booth were examples of some entirely new and strange use of copper sulfate, such as in the curing of human hair for hair nets, or the fireproofing of theatrical hangings, if either were possible. Properly displayed, such processes would coax in interested visitors far more readily than the simple exhibit of a few bottles and kegs of well-known products of this material.

Here, then, is the germ of the idea which will bring interested buyers to the point of at least leaving their names, if not actually signing on the dotted line—*get their interest by something new*. We think of many new developments which could have been shown to advantage, and as proof of our contention we cite the exhibit of the American dye industry and that of the AMERICAN CHEMICAL SOCIETY, both of which presented old ideas in entirely new ways, so far as the exposition was concerned. True, neither of these booths was designed to *sell* definite products, but it is equally true that these two booths competed with endless exhibits of machinery in motion, and most successfully. The chemical manufacturers can do the same if they will only confine their efforts to new ideas or new ways of presenting old ones, instead of endless arrays of specimens of products with which the entire chemical world is perfectly familiar. The whole scheme of the exposition cannot be justly criticized for the failure of exhibitors to take full advantage of their opportunities.

# Some Factors Influencing the Design of Absorption Apparatus<sup>1</sup>

By R. T. Haslam, W. P. Ryan, and H. C. Weber

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

IN THE design of an absorption system we are usually concerned with the size of tower or scrubber necessary to absorb a given amount of material per hour under fixed terminal conditions—e. g., concentration of entering gas, temperature of scrubbing liquid, per cent recovery, etc. Oftentimes, in addition, it is desirable to know how a change in one or more of these terminal conditions will affect either the size unit required, the capacity of a given unit, or the per cent of material lost in the exit gases. Both problems involve the rate at which matter is transferred from a gas to a liquid or vice versa. Here, as in the cases of the flow of electricity and the flow of heat, the rate of transfer is proportional to a "driving force." In the flow of heat this driving force is the temperature difference between the hot and the cold body; in electricity the driving force is the potential difference or e. m. f. existing between the two points; in absorption it is the distance the gas-liquid system is from equilibrium. In the case of the flow of electricity the resistance also influences the quantity of electricity that will flow in a given time. With the transfer of heat the same situation holds true—the amount of heat that flows from a hot body to a cold one in a unit time is not only proportional to the temperature difference (driving force), but it is also inversely proportional to the resistance through which the heat must flow. So, too, with the transfer of material in absorption apparatus, the rate of flow of the material from one phase to the other is not only proportional

<sup>1</sup> Received August 27, 1923. Revised from a paper presented at the meeting of the American Institute of Chemical Engineers, Richmond, Va., December 6 to 9, 1922.

*The advisability of studying absorption by methods successfully used in the study of the similar and related field, flow of heat, is pointed out.*

*The effect of the two resistances, the "gas film" and the "liquid film," is shown by studying the effect of gas velocity or the absorption of sulfur dioxide by water. The gas-film resistance appears to be proportional to the gas velocity to the 0.8 power. The liquid-film resistance appears to be practically independent of the gas velocity. The over-all coefficient of absorption rises rapidly with an increase in gas velocity reaching an asymptote due to the comparatively stationary liquid-film resistance.*

*The equations connecting the rate of absorption with gas velocity are given.*

to the driving force (distance the system is from equilibrium), but it is also inversely proportional to the resistances in between the gas and liquid—namely, as shown by Whitman and Keats,<sup>2</sup> the gas film and the liquid film. These film resistances are not due to actual stationary films through which heat flows by conduction and material by diffusion, but in both cases at present these resistances

are considered as equivalent to stationary films of varying thickness.

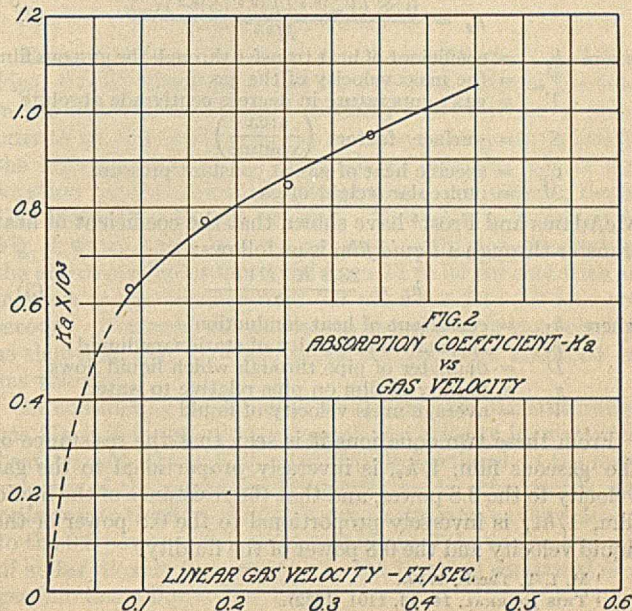
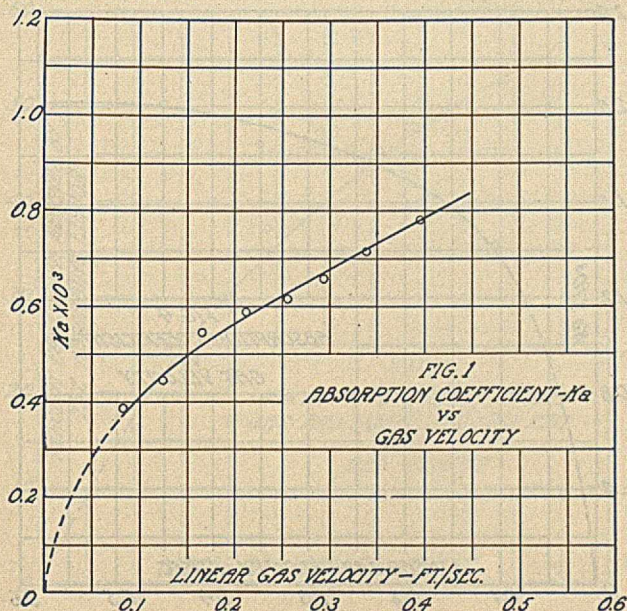
The similarity between the flow of heat and the transfer of material from a gas to a liquid phase, or vice versa, does not end with the fact that each is proportional to a driving force and inversely proportional to a resistance. It has been shown also that the major resistances in both cases are equivalent to film resistances, gas and liquid films, and, in addition, W. K. Lewis<sup>3</sup> has shown that under certain limiting conditions the coefficient of material transfer is proportional to the coefficient of heat transfer. In view of this similarity it seems advisable to study the rate of absorption (or transfer of material from gas to liquid) in a manner similar to the study of the older science, the flow of heat. Newton's law on the flow of heat is as follows:

$$\frac{dQ}{d\theta} = \left(\frac{hA}{dl}\right) dt \quad (1)$$

where  $dQ/d\theta$  is the quantity of heat flowing per unit of time through the area  $A$  of thickness,  $dl$ , when the driving force or temperature difference is  $dt$ . The constant  $h$  is the coeffi-

<sup>2</sup> THIS JOURNAL, 14, 186 (1922).

<sup>3</sup> Mech. Eng., 44, 445 (1922).



cient of heat conductivity. This equation has the same form as Ohm's law, where

$$\text{Quantity (current)} = \frac{\text{Driving force (e. m. f.)}}{\text{Resistance}}$$

where  $dQ/d\theta$  is the quantity factor,  $dt$  the driving force, and  $dl/hA$  is the resistance. In the transfer of heat  $1/h$  is the total or over-all coefficient of resistance, often composed of three resistances, the intervening wall, and the fluid film resistances on either side of the wall. An exact knowledge of

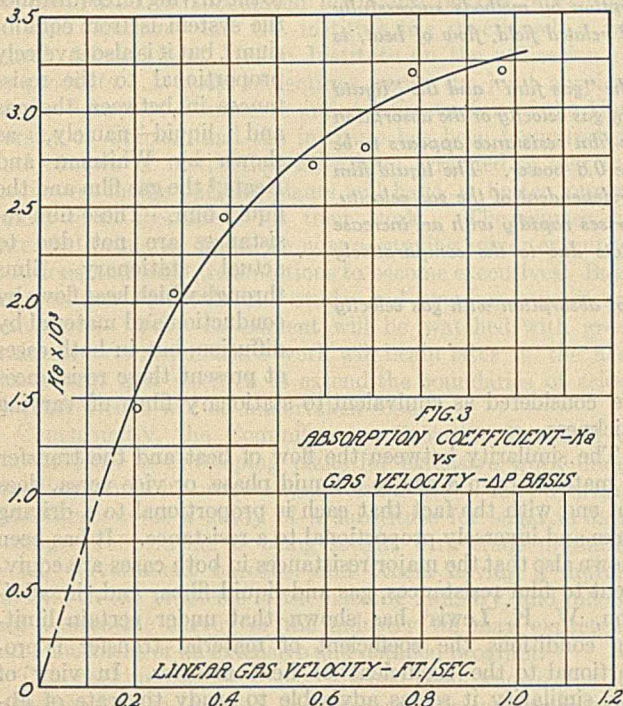


FIG. 3  
ABSORPTION COEFFICIENT- $Ka$   
VS  
GAS VELOCITY- $\Delta P$  BASIS

the laws governing the flow of heat was brought about, not by investigating the over-all coefficient of resistance,  $1/h$ , but by determining the coefficients of resistance of the walls and the films separately and noting how such variables as materials, velocity, temperature, etc., changed each resistance. Knowing each of the resistances, one may easily calculate the over-all resistance. In heat transfer the main problem is the determination of the two film coefficients. As shown by Weber<sup>4</sup> the coefficient of heat transfer for gaseous films (forced convection) is as follows:

$$h_g = \frac{0.88 (V_m)^{0.8} (T)^{0.5} (S)^{0.2} (C_p)}{M^{0.3}} \quad (2)$$

where  $h_g$  = coefficient of heat transfer through the gaseous film  
 $V_m$  = the mass velocity of the gas  
 $T$  = gas temperature in degrees centigrade absolute  
 $S$  = surface factor  $\left(\frac{\text{area}}{\text{volume}}\right)$   
 $C_p$  = specific heat of gas at constant pressure  
 $M$  = molecular weight of gas

McAdams and Frost<sup>5</sup> have shown that the coefficient of heat transfer through a liquid film is as follows:

$$h_L = \frac{23.3 K (DV_z)^{0.8}}{D} \quad (3)$$

where  $h_L$  = coefficient of heat conduction  
 $K$  = thermal conductivity of stationary liquid  
 $D$  = diameter of pipe through which liquid flows  
 $z$  = fluidity of film on pipe relative to water  
 $V$  = average mass velocity of liquid

From these two equations it is seen that the resistance of the gaseous film,  $1/h_g$ , is inversely proportional to the gas velocity to the 0.8 power, and that the resistance of the liquid film,  $1/h_L$ , is inversely proportional to the 0.8 power of the liquid velocity and the 0.8 power of the fluidity.

<sup>4</sup> M. I. T. Thesis, 1919.

<sup>5</sup> THIS JOURNAL, 14, 13, 1101 (1922).

Turning now to material transfer or absorption, the rate of absorption of one material from a stream by another stream of material flowing countercurrent to the former may be expressed in a manner similar to the flow of heat (Equation 1).

$$\frac{dW}{d\theta} = ka V \Delta P \quad (4)$$

where  $\frac{dW}{d\theta}$  = weight in pounds of material being absorbed per minute

$\Delta P$  = driving force or distance from equilibrium, often expressed as pressure difference between the partial pressure of solute in gaseous and liquid phases, expressed in millimeters of mercury

$V$  = total interior volume of apparatus in cubic feet

$ka$  = over-all absorption coefficient equivalent to the pounds of gas absorbed per minute per cubic foot of volume per millimeter mercury partial pressure difference when  $\Delta P$  and  $V$  are expressed as above

This differential may be expressed as an average equation of rate

$$\frac{W}{\theta} = ka V (\Delta P)_{av.} \quad (4a)$$

When the gas obeys Henry's law and the temperature effects are small, the  $\Delta P_{av.}$  is the logarithmic mean of the pressure differences between the partial pressure of the solute in the gaseous and liquid phases taken at the ends of the system. In this equation the over-all coefficient of absorption,  $k$ , is coupled with the unknown area through which absorption takes place,  $a$ . The over-all coefficient,  $ka$ , is proportional to  $\frac{1}{R_g + R_L}$ , where  $R_g$  is the resistance of the gas film and  $R_L$  is the resistance of the liquid film.

The following experimental work absorbing sulfur dioxide from burner gas by water was carried out with the view of studying the effect of gas velocity and temperature on the rate of absorption, with the hope thereby to obtain more information regarding the nature of the film resistance and to see if the resultant over-all coefficient of absorption,  $ka$ , could be explained on the basis of two films, gaseous and liquid, in series each obeying a law similar to that governing the flow of heat through similar films.

#### EXPERIMENTAL RESULTS

Series I was made with an unpacked tower 8 inches in diameter by 30 inches high, through which water was fed down the inside wall at a rate equivalent to 16.8 pounds per square foot of cross-sectional area per minute at a constant

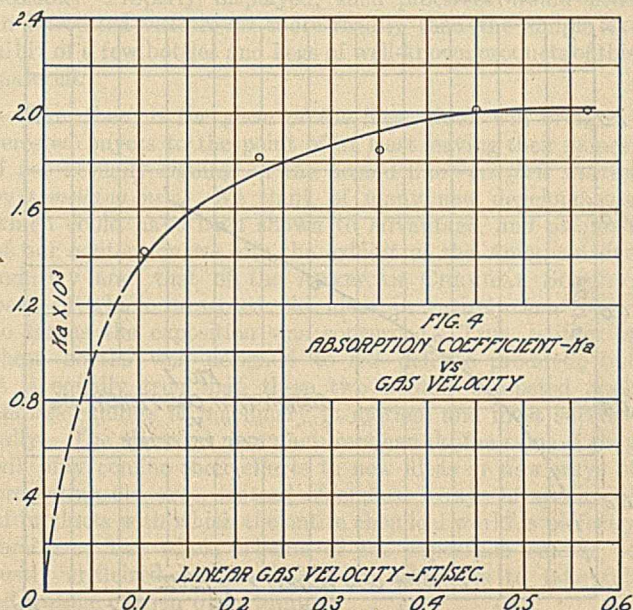
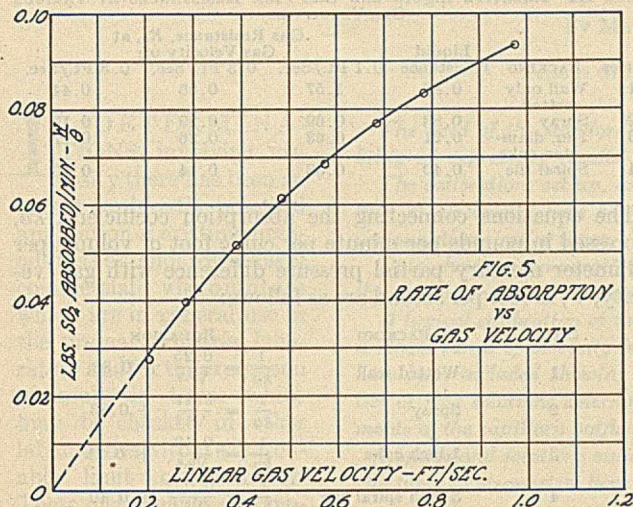


FIG. 4  
ABSORPTION COEFFICIENT- $Ka$   
VS  
GAS VELOCITY

temperature of approximately 58° F. The velocity of the gas was varied from 0.084 foot per second to 0.396 foot per second, and the rates of absorption, absorption coefficient,



and per cent absorption are given in Table I. The absorption coefficient is plotted vs. gas velocity in Fig. I.

TABLE I—RATE OF ABSORPTION VS. GAS VELOCITY

Gas Velocity Ft./Sec.	$ka \times 10^3$	Lbs. SO <sub>2</sub> Absorbed/Min. $\frac{dW}{d\theta}$	$\Delta P$ Mm. Hg	Per cent of Total SO <sub>2</sub> Absorbed
Series 1				
0.084	0.39	0.0134	39.2	47.3
0.125	0.44	0.0162	42.0	40.5
0.166	0.55	0.0204	42.5	30.0
0.213	0.59	0.0208	40.5	31.6
0.256	0.61	0.0221	41.5	30.0
0.294	0.66	0.0252	43.7	26.0
0.339	0.71	0.0270	43.5	24.5
0.396	0.78	0.0286	42.0	17.0
Series 2				
0.088	0.63	0.0225	41.1	68
0.167	0.77	0.0304	45.2	49
0.254	0.85	0.0382	51.5	34
0.341	0.95	0.0438	52.8	30

Series 2 was made in the same tower as Series 1, but the water was sprayed in at the rate of 32.6 pounds per square foot of cross section per minute. The temperatures were approximately constant at 55° F. The gas velocity was varied from 0.088 foot per second to 0.341 foot per second. The resultant data similar to that taken in Series 1 are shown in Table I, and in Fig. 2  $ka$  is plotted against gas velocity.

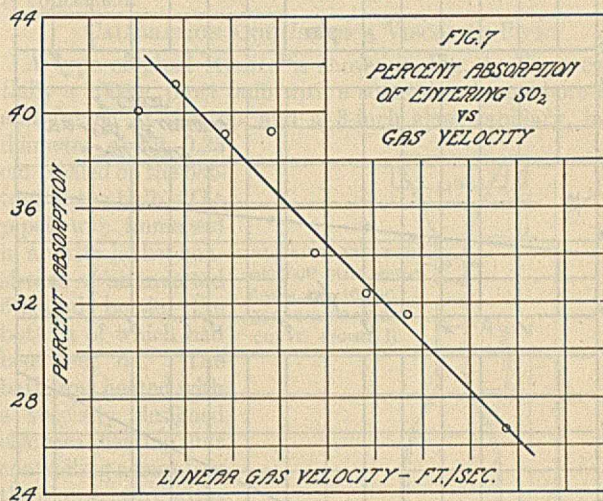
Series 3 was made with the same tower packed with 1-inch

diameter coke, the water rate being 32.3 pounds per square foot of cross section per minute and the temperature approximately 56° F. The gas velocity was varied from 0.204 to 0.976 foot per second and the results are shown in Table III and in Fig. 3 the absorption coefficient,  $ka$ , is plotted against gas velocity.

TABLE II—EFFECT OF LINEAR GAS VELOCITY ON ABSORPTION

Gas Velocity Ft./Sec.	$ka \times 10^3$	Lbs. of SO <sub>2</sub> Absorbed/Min. $\frac{dW}{d\theta}$	$\Delta P$ Mm. Hg	Per cent SO <sub>2</sub> Absorbed	Per cent Equilibrium Reached
Series 3					
0.204	1.46	0.0278	21.8	40.1	16.2
0.282	2.06	0.0398	22.2	41.2	24.3
0.389	2.45	0.0516	24.0	39.1	30.0
0.484	2.71	0.0614	26.2	39.2	37.2
0.578	2.72	0.0686	29.1	34.1	39.0
0.684	2.79	0.0770	31.4	32.4	43.8
0.785	3.17	0.0833	30.1	31.6	48.3
0.976	3.18	0.0933	33.2	26.7	52.8
Series 4					
0.113	1.41	0.0256	20.8	92.0	15.8
0.223	1.81	0.0480	30.3	77.7	28.4
0.352	1.84	0.0627	39.0	61.1	35.0
0.449	2.06	0.0688	38.1	50.5	40.5
0.565	2.02	0.0694	39.4	47.7	40.2

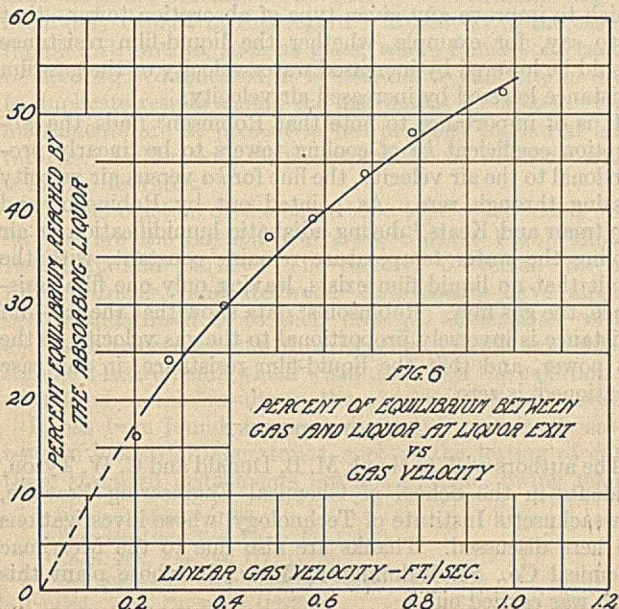
Series 4 was made with a tower 8 inches in diameter, 30 inches high, packed with 3 x 3-inch spiral tile, the water rate being 32.1 and the temperature approximately 60° F. The gas velocity was varied from 0.1 foot per second to 0.565 foot per second. The results are given in Table II, and in Fig. 4 the absorption coefficient,  $ka$ , is plotted against gas velocity.



## DISCUSSION OF RESULTS

EFFECT OF GAS VELOCITY—In all cases (Series 1 to 4 and Figs. 1 to 4, inclusive) it will be seen that with an increase in gas velocity  $ka$  increases probably from zero (or a point near to it) at a rapid rate, the increase in  $ka$  growing less at the high gas velocities. Fig. 5 shows how the rate of absorption (pounds sulfur dioxide absorbed per minute, Series III) increases with gas velocity. This also is indicated in Fig. 6, which shows how the per cent equilibrium reached by the absorbing liquor increased from 15 to 52 per cent with an increase in gas velocity from 0.2 foot per second to 1.0 foot per second. However, the exit losses increase with gas velocity, as shown in Fig. 7, which gives the per cent absorbed vs. gas velocity.

In considering Equation 2 for the transfer of heat through gas films, it is seen that increased gas velocity increases the heat transfer through the gas film proportional to the mass velocity of the gas to the 0.8 power, or, in other words, the resistance to the flow of heat decreases *inversely* as the velocity to the 0.8 power. Now if the resistance  $1/ka$  to the transfer of sulfur dioxide from the gas to the liquid is composed of a gas film and a liquid film, then



$$\frac{1}{ka} = R_g + R_L$$

Assuming that the gas resistance varies inversely as the gas velocity and that gas velocity has no effect on the liquid film, we have

$$\frac{1}{ka} = \frac{C}{V^{0.8}} + R_L \quad (5)$$

$ka$  = absorption coefficient       $C$  = constant  
 $V$  = gas velocity                       $R_g$  = gas-film resistance  
 $R_L$  = liquid-film resistance

Whitman and Keats<sup>2</sup> do not consider the liquid film to be unaffected by gas velocity, while Robinson<sup>6</sup> finds otherwise. Fig. 8 shows  $1/ka$  plotted against  $1/V^{0.8}$  for Series 1 to 4, inclusive, the points falling close to straight lines as one would expect if Equation 5 is correct. Based on these assumptions, the relative liquid-film resistance and the gas-film resistance

<sup>6</sup> Mech. Eng., 45, 99 (1923).

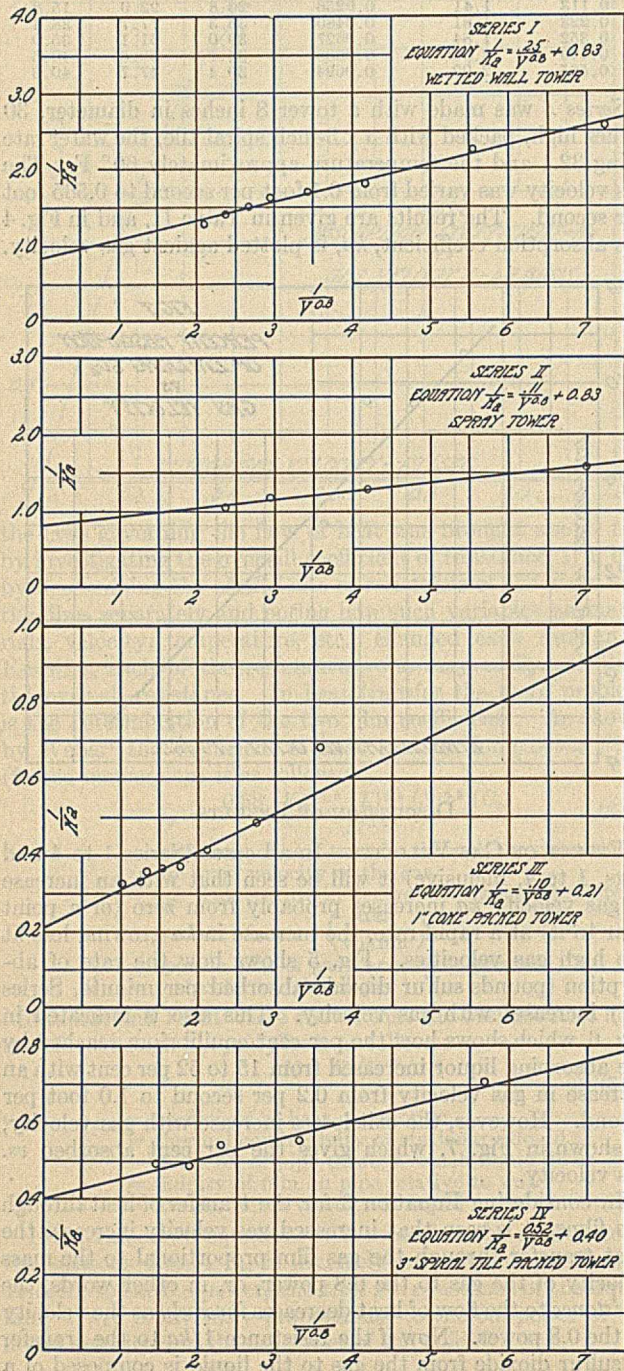


FIG. 8

at different velocities were computed and the results are shown in Table III.

TABLE III—RELATIVE LIQUID AND GAS FILM RESISTANCES AT VARIOUS GAS VELOCITIES

Series	PACKING	Liquid Resistance	Gas Resistance, $R_g$ , at Gas Velocity of:	
			0.1 Ft./Sec.	0.3 Ft./Sec.
1	Wall only wetted	0.83	1.57	0.66
2	Spray	0.83	0.69	0.29
3	1-in. diameter coke	0.21	0.63	0.26
4	Spiral tile	0.40	0.33	0.14

The equations connecting the absorption coefficient,  $ka$ , expressed in pounds per minute per cubic foot of volume per millimeter mercury partial pressure difference with gas velocity,  $V$ , in feet per second are as follows:

Series	PACKING	EQUATION
1	Wetted wall	$\frac{1}{ka} = \frac{0.25}{V^{0.8}} + 0.83$
2	Spray	$\frac{1}{ka} = \frac{0.11}{V^{0.8}} + 0.83$
3	1-inch coke	$\frac{1}{ka} = \frac{0.10}{V^{0.8}} + 0.21$
4	3-inch spiral tile	$\frac{1}{ka} = \frac{0.052}{V^{0.8}} + 0.40$

The first term on the right-hand side of the equations is the gas resistance term, while the second refers to the water resistance. In Series 2, 3, and 4 the water rate was constant at approximately 32 pounds water per square foot per minute, while in Series 1 it was 17 pounds.

It is to be noted that the liquid-film resistances follow the order of magnitude one would expect—namely, that it is least with the 1-inch coke-packed tower and greater with the spray and wetted-wall type of tower. The spiral-packed tower is intermediate in this respect between spray and the coke-filled towers. From an inspection of Table III and Figs. 1 to 4, inclusive, and Fig. 8, it can be said that the data show the effect of the two films, the effect of gas velocity at low gas velocities being great since the main resistance is the gas film, whereas at high gas velocities the effect is due to the increasing importance of the fairly constant liquid film. Furthermore, these data indicate why increased gas velocity has such a small effect on the absorption coefficient of spray type of towers—namely, that the liquid-film resistance, which is fairly constant with increasing gas velocity, is the major resistance, in addition to the gas resistance being excessively high due to "slippage" between the gas and liquid. This treatment shows quickly the line of attack along which to improve any given type of absorption tower—that is to say, for example, whether the liquid-film resistance should be lowered by increased water velocity or the gas-film resistance lowered by increased air velocity.

It is of importance to note that Robinson<sup>6</sup> finds the absorption coefficient  $ka$  of cooling towers to be linearly proportional to the air velocity, the line for  $ka$  versus air velocity passing through zero. As pointed out by Robinson<sup>6</sup> and Whitman and Keats,<sup>2</sup> during adiabatic humidification or air cooling the water temperature remains constant, with the result that no liquid film exists, leaving only one film resistance, the gas film. Robinson's<sup>6</sup> data show that the gas-film resistance is inversely proportional to the gas velocity to the 0.8 power, and that the liquid-film resistance, in the case mentioned, is zero.

ACKNOWLEDGMENT

The authors wish to thank M. B. Donald and C. W. Tyson, students in the School of Chemical Engineering Practice, Massachusetts Institute of Technology, whose investigations are here discussed. Thanks are also due to the Merrimac Chemical Co., So. Wilmington, Mass., in whose plant this work was carried out.



# The Standardization of Commercial Viscometers<sup>1</sup>

By Madison L. Sheely

ARMOUR GLUE WORKS, CHICAGO, ILL.

**I**N DETERMINATIONS involving viscosity there has been an urgent need for the practical application of existing methods to the standardization of commercial viscometers which are in general use in the present industrial laboratory and for the expression of results in terms which may be checked in other laboratories within a reasonable limit of accuracy. These instruments are generally constructed of glass of varying shapes and dimensions, and the results of tests on them are never strictly comparable, owing to these variations and the impossibility of exactly reproducing the critical dimensions in glass. To be sure, various methods of calibration of most "standard" commercial instruments are now available. We have, then, only to select the method which is most suited to the type of instrument available, and by careful determinations on liquids of known viscosities, covering the range in which the viscometer is to be used, to obtain a calibration curve for that particular instrument. Obviously, this method of calibration is the only one available with instruments of the type where dimensions are not known.

A calibration of this kind serves two definite purposes. In the first place it expresses the results in absolute units, a system which cannot be too highly recommended. The expression of viscosity in arbitrary units, such as seconds of outflow or degrees MacMichael, or in relations such as the ratio of time of outflow to the time of outflow for water, is entirely inadequate and very confusing, especially with instruments of the type described above. Secondly, the results may be duplicated in separate laboratories. Materials which are purchased on viscosity specifications may be accurately defined in this regard. Moreover, in the case of fragile instruments, such as glass, where dimensions cannot be accurately duplicated, it is essential to calibrate in order to duplicate results should the instrument be broken. Such instruments are at present in use in many industrial laboratories. Calibration, then, especially in absolute units, is highly desirable.

The viscometers of the short tube type most widely used for oils are the Saybolt Universal, Saybolt Furol, Engler, Redwood, and Barbey. The Saybolt Universal,<sup>2</sup> Saybolt Furol,<sup>3</sup> Engler,<sup>4</sup> and Redwood<sup>5</sup> instruments have already been standardized as to their principal dimensions, within allowable tolerances, and thus have been made available as standard instruments which when used with the equation for each type express results in the absolute unit of viscosity.

It has been found, however, that with certain classes of tests in industrial laboratories, such as the testing of glues, these standard instruments are not suitable, owing mainly

*The need of the standardization of viscometers, and the advisability of expressing results in absolute units has been discussed.*

*The calibration, set up, and operation of a typical glass outflow type of viscometer have been given, together with comparisons of various other similar types.*

*Data showing comparative results of viscosity determinations on the various instruments are given.*

*A typical calibration of the MacMichael torsional viscometer for a single range of viscosity has been studied and comparative data have been included showing unexplained discrepancies in viscosities of glue solutions determined by this instrument and by instruments of the capillary outflow type.*

*Liquids and solutions suitable for the standardization of commercial types of viscometers have been briefly discussed.*

to the fact that the difference in results of tests from the lowest to the highest grades is not great enough clearly to define the many grades which must be designated between them. This so-called "spread" from one grade of glue to the next is especially narrow on the low viscosity glues. For this reason mainly, other instruments of various types, usually of glass and with a much longer capillary (to increase the spread), are

commonly employed. It is with the typical calibration of several of these types, together with a typical calibration of the MacMichael torsional viscometer, that this investigation is concerned.

## CALIBRATION AND USE OF A VISCOSITY PIPET

A type of pipet studied is shown in Fig. 1. It is essentially a 100-cc. pipet bulb with a somewhat larger bore tube and funnel at the top, and a 3-inch glass capillary, inside diameter about 0.25 cm., sealed on the bottom of the bulb. The pipet was immersed in a water jacket consisting of an inverted 5-pound bottle, the bottom of which had been cut off. The bath was heated with a specially designed electrical heating unit controlling accurately the temperature within  $\pm 0.1^\circ\text{C}$ ., agitation being effected by means of a slow current of compressed air.

The general method of procedure was to bring the temperature of the liquid to be tested slightly above or below the desired temperature, according to whether the temperature of the determination was above or below that of the room, and after pouring into the pipet to adjust it by means of an accurately graduated thermometer. A slight stirring was effected by moving the thermometer up and down within the pipet. When the desired temperature was reached, the thermometer was withdrawn and the head adjusted to an etched line, A, located on the upper tube, and the time

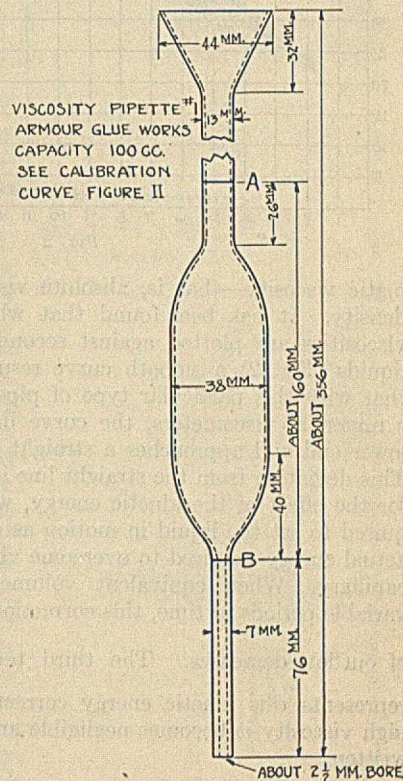


FIG. 1

<sup>1</sup> Received May 21, 1923.

<sup>2</sup> *Bur. Standards, Tech. Paper*, 112 (1919).

<sup>3</sup> *Chem. Met. Eng.*, 26, 1175 (1922).

<sup>4</sup> *Bur. Standards, Tech. Paper* 100 (1917); 112 (1919).

<sup>5</sup> *Ibid.*, *Tech. Paper* 210 (1922).

measured from this point to another etched line, *B*, at the top of the capillary tube.

The general equation for viscosity for any given instrument, the critical dimensions of which are unknown and depend on flow due to gravity, is

$$\frac{\mu}{\gamma} = At - \frac{B}{t} \quad (1)$$

in which  $\mu$  is the absolute viscosity in centipoises,  $\gamma$  is the density in grams per cubic centimeter,  $t$  is the time of outflow in seconds, and  $A$  and  $B$  are constants of the given instrument. The first term,  $\frac{\mu}{\gamma}$ , is usually designated as kine-

matic viscosity with respect to the kinematic viscosity curve depending on whether they have a density greater or less than one; but when these values are changed over to the corresponding kinematic viscosities the continuous kinematic curve shown is obtained.

There are several methods<sup>2</sup> of finding the two constants  $A$  and  $B$  in Equation 1. The method used in the calibration of these pipets consists in finding the time of discharge of two liquids of known widely different viscosities. These values of  $t$ , together with the known corresponding values of  $\mu$  and  $\gamma$ , are then substituted in Equation 1. The two simultaneous equations are then solved for  $A$  and  $B$ . In order to check the relation between kinematic viscosity and time thus found, several other solutions of intermediate, known viscosities were run and found to check remarkably well with the values calculated. (Fig. 2 and Table I) The liquid of lower viscosity must be so selected that the type of flow is still viscous—that is, in straight-line motion, since the equation does not hold true when the flow is turbulent.

TABLE I—VISCOSITIES OF SOLUTIONS COMPARED WITH CALCULATED VISCOSITIES DETERMINED WITH PIPET 1

( $A = 0.1807$ ;  $B = 54.0$ )

Temperature C.	Seconds	Centipoises	Kinematic Viscosity	Calculated	Error
<i>Medicinal Paraffin Oil</i>					
30	104.0	15.15	18.27 <sup>a</sup>	18.27	0.00
45	64.8	8.96	10.92	10.89	0.03
60	46.2	5.87	7.22	7.18	0.04
<i>25 Per cent Glycerol</i>					
20	23.9	2.18	2.06 <sup>a</sup>	2.06	0.00
<i>45 Per cent Glycerol</i>					
20	32.8	4.69	4.22	4.27	0.05
<i>Water</i>					
30	19.2	0.80	0.81	0.66	0.15
<i>60 Per cent Sucrose</i>					
65	43.0	8.34	6.61	6.52	0.09
60	48.2	9.83	7.77	7.58	0.19
55	56.2	11.67	9.26	9.20	0.06
50	65.0	14.01	11.03	10.89	0.14
45	77.0	17.18	13.49	13.20	0.29
<i>40 Per cent Sucrose</i>					
60	22.8	1.98	1.71	1.76	0.05
40	27.2	3.25	2.78	2.94	0.16
35	28.8	3.76	3.22	3.33	0.11
30	30.6	4.38	3.74	3.76	0.02
25	33.5	5.19	4.42	4.44	0.02
20	37.2	6.20	5.27	5.27	0.00
15	42.0	7.47	6.34	6.31	0.03
<i>44.11 Per cent Ethyl Alcohol (by Weight)</i>					
30	24.6	2.02	2.18	2.25	0.07
<i>60 Per cent Glycerol</i>					
20	55.0	10.31	8.96	8.86	0.10
<i>Castor Oil</i>					
40	1349.4	231.0	244.0	243.7	0.30

<sup>a</sup> These two values were used in calculating the  $A$  and  $B$  constants in Equation 1.

matic viscosity—that is, absolute viscosity divided by the density. It has been found that when known kinematic viscosities are plotted against seconds of outflow of these liquids (Fig. 2) a smooth curve results. It will be noted that with this particular type of pipet, as with most other commercial viscometers, the curve bends slightly near the lower end and approaches a straight line at the upper end. This deviation from the straight line is due to the correction for the effect of the kinetic energy, which is the energy required to set the liquid in motion as distinguished from the actual energy required to overcome viscous resistance in the capillary. When equivalent volumes are delivered over variable periods of time, this correction increases as the time

of outflow decreases. The third term,  $\frac{B}{t}$ , of Equation 1 represents this kinetic energy correction. With liquids of high viscosity it becomes negligible and Equation 1 may be written

$$\frac{\mu}{\gamma} = kt \quad (2)$$

which indicates that kinematic viscosity in these cases is directly proportional to the time. It will be noted also on Fig. 2 that when seconds of outflow of the same liquids at the various temperatures are plotted against the absolute viscosity in centipoises, for each of the three calibrating liquids used three separate and distinct curves are obtained,

To determine the absolute viscosity, then, of any unknown liquid, it is necessary to determine the time of discharge and from a calibration curve or by calculation from the  $A$  and  $B$  constants in Equation 1 to obtain the kinematic viscosity. This value multiplied by the density at the temperature of the test gives the absolute viscosity in centipoises.

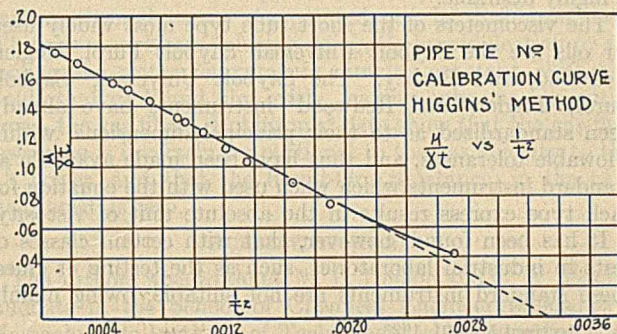


FIG. 3

A graphical method for the determination of the  $A$  and  $B$  constants in Equation 1 for any given instrument has been

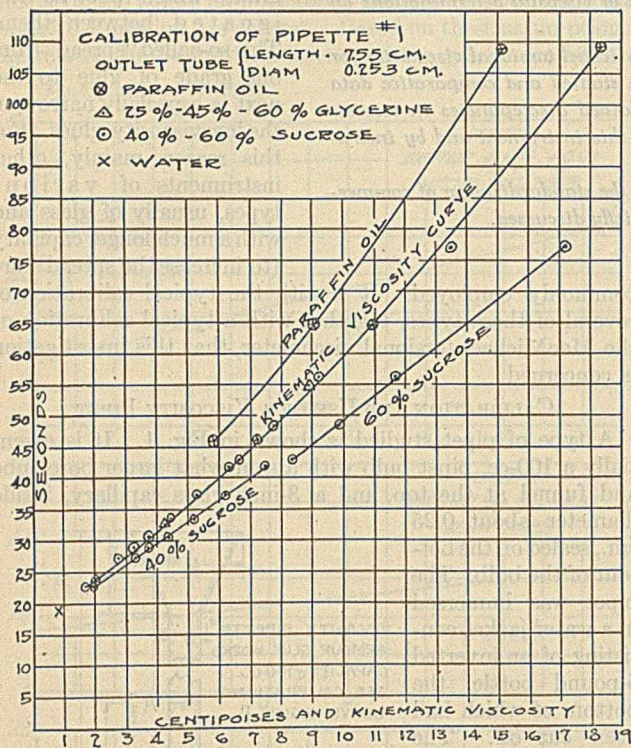


FIG. 2

evolved by Higgins.<sup>6</sup> He combines Equations 1 and 2

$$k = \frac{\mu}{\gamma t} = A - \frac{B}{t^2}$$

and plots the values  $\frac{\mu}{\gamma t}$  against  $\frac{1}{t^2}$ . The data given in

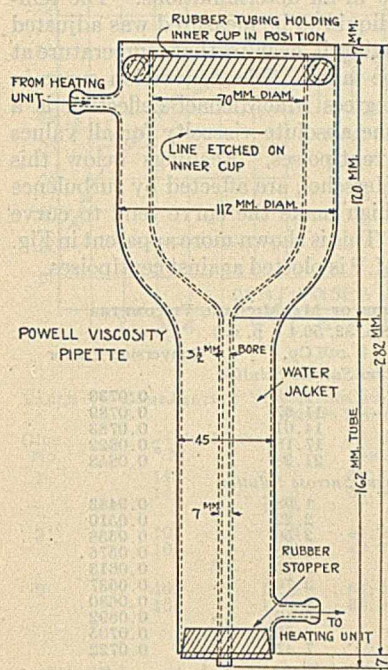


FIG. 4

to bend upwards. From the value of  $\frac{1}{t^2}$ , at which this break occurs, may be calculated, approximately, the number of seconds of outflow below which the instrument may not be used and which is near the region of critical velocity—that is, the region of change from viscous to turbulent flow. The position of this region varies with the dimensions of the capillary, but in general the shorter the capillary the lower will be the velocity at which turbulence begins. It is of utmost importance in the calibration of any instrument of this general type to determine, at least approximately, this region of change of flow. It may not be possible to obtain the exact point, but a point well below the critical velocity may easily be selected for use in determining the constants. This, in fact, was the manner in which Pipet 1 was calibrated, as only one point (for water) above the critical velocity was obtained and the exact point at which the critical velocity was exceeded was not accurately determined. With velocities above this region, only the particles nearest the walls of the capillary are moving in parallel motion, while the main volume is in violent, turbulent action.

When the value of the expression  $\frac{vd\gamma}{\mu}$ , generally known as Reynold's criterion, exceeds a certain figure which is characteristic of each type of viscometer, the change from parallel to turbulent flow has taken place. An attempt has been made to calculate the value of this criterion for the region of critical velocity, but owing to the non-uniformity of the diameter of the glass capillary and other dimensions, an approximation only could be arrived at. For Pipet 1 this region lies near to the value  $\frac{vd\gamma}{\mu} = 12.00$ , which is less than the value 20.00 generally used with the long tube instruments, since the capillary is only 30.5

Table I for Pipet 1 were used in plotting these values in Fig. 3. The *A* factor, then, is numerically equal to the intercept of the line on the axis of ordinates, while the *B* factor is equal to the tangent of the angle which the straight portion of the line, extended to the axis of abscissas, makes with that axis. This method has the advantage that it aids in selecting a suitable calibrating liquid for the low point on the curve, as it is thereby possible with most types to obtain a series of points near the lower end which will indicate where the straight line begins to break, giving high values for  $\frac{\mu}{\gamma t}$  and causing the line

diameters in length, and is greater than the value 8.00, which is the value calculated for instruments of the short tube type, such as the Engler and Saybolt,<sup>4</sup> where the ratio of length to diameter is about 7.

If only a limited degree of accuracy is desired, the point of critical velocity may be obtained by calculating the *A* and *B* constants from a series of low points and a single high point and selecting the pair which will give a correct calculation for a value on the curve immediately below the selected point. For instance, if values for *A* and *B* are calculated from a 45 per cent solution of glycerol and a suitable high point and these values suffice to calculate the known viscosity of a 40 per cent solution of glycerol, then it is reasonable to assume that the *A* and *B* values are correct. The constants, however, may not be used to calculate viscosities above the critical velocity. About forty pipets of the type described above have been calibrated in this manner, and solutions of unknown viscosities have been evaluated to an accuracy of less than  $\pm 0.1$  centipoise. Table II gives a series of viscosity determinations on glue solutions (12.5 per cent, 60° C.) on two pipets calibrated by this method. Portions of the same solution were used with each pipet in order to eliminate any error due to concentration or method of preparation. Pipet 2 was of the same type as Pipet 1, but the running time was considerably less.

TABLE II—VISCOSITY OF GLUE SOLUTIONS DETERMINED BY TWO PIPETS

Glue No.	Pipet 1 Cp.	Pipet 2 Cp.	Difference Cp.
1	15.86	15.97	0.11
3	13.73	13.72	0.01
5	11.83	11.88	0.05
7	10.26	10.11	0.15
9	8.64	8.59	0.05
11	7.40	7.42	0.02
13	6.32	6.24	0.08
15	5.28	5.35	0.07
17	4.46	4.50	0.04
19	3.74	3.73	0.01
21	3.17	3.18	0.01

In order to determine the suitability of a pipet for a given range of viscosity, two other pipets of radically different design were calibrated. The Powell pipet shown in Fig. 4 consists of a cup-shaped glass vessel with attached glass capillary  $5\frac{16}{16}$  inches in length, the whole surrounded by a glass water bath. The initial head was adjusted by means of an etched line on the upper part of the cup and the volume delivered was measured by means of an ordinary 200-cc. Engler volumetric flask. The third type of pipet calibrated, which was kindly furnished by George R. Underwood of The American Glue Company, is shown in Fig. 5 and is similar

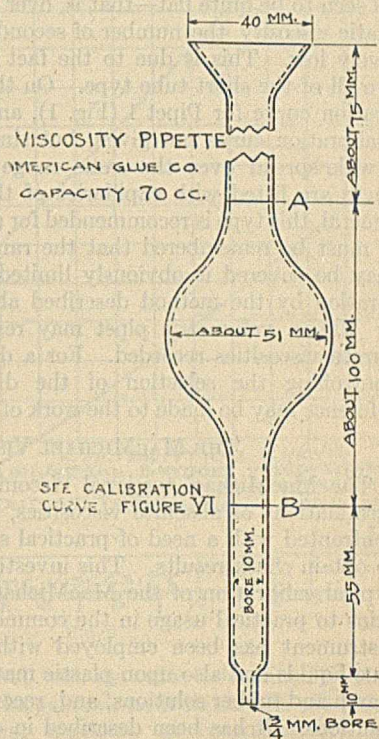


FIG. 5

to one shown in Fig. 1 except that the capillary is only 10 mm. long and about 1.75 mm. in diameter. Moreover, the volume delivered was only 70 cc. instead of 100 cc. The *A* and *B* constants for each of these instruments were

<sup>6</sup> Collected Researches, The National Physical Laboratory, 11. (1914).

determined and the viscosity of portions of the same gelatin solution determined on each, with the results indicated in Table III.

VISCOMETER	Seconds	Calculated Absolute Viscosity Cp.
Pipet 1	77.4	13.55
Pipet 2	71.4	13.56
Powell Cup Pipet	74.8	13.61
American Glue Company Pipet, 70 Cc.	59.4	13.94

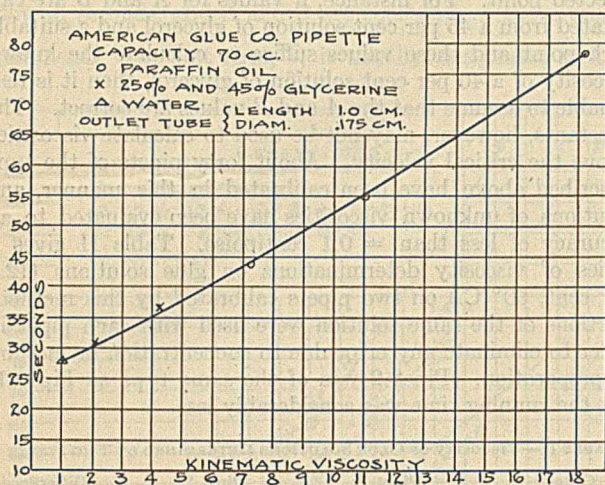


FIG. 6

**FACTORS CONTROLLING THE SELECTION OF A PIPET**—The calibration curves of the various types of pipets, together with those of the Saybolt and Engler, are sufficient to indicate the importance of the suitability of these types for any particular viscosity determination. The curves for the Engler, Saybolt, and the American Glue Company's pipet are all seen to be quite flat—that is, over the same range of kinematic viscosity the number of seconds "spread" is comparatively low. This is due to the fact that these viscometers are all of the short tube type. On the other hand, the calibration curve for Pipet 1 (Fig. 1), and also the Powell pipet (calibration curve not given, but similar to Pipet 1), shows a wide spread over the same range of viscosity. Both of these are fitted with capillaries of the long tube type. In general, this type is recommended for accurate work, although it must be remembered that the range of viscosities which may be covered is obviously limited. The emergency calibration by the method described above of an ordinary 50 or 100-cc. volumetric pipet may readily be made and accurate viscosities recorded. For a discussion of the factors controlling the selection of the dimension of capillaries reference may be made to the work of Bingham.<sup>7</sup>

#### THE MACMICHAEL VISCOMETER

The MacMichael torsional viscometer lends itself to determinations of absolute viscosities, but here again we are confronted with a need of practical standardization in order to obtain check results. This investigation has considered a typical calibration of the MacMichael viscometer as it pertains to practical usage in the commercial laboratory. This instrument has been employed with success upon various true liquids and also upon plastic material such as slip clays, starch and rubber solutions, and, recently by Bogue,<sup>8</sup> on glue solutions. It has been described in detail by MacMichael,<sup>9</sup> Herschel,<sup>10</sup> Hayes and Lewis,<sup>11</sup> and the reader is referred to

these publications for a complete discussion and calibration of the MacMichael viscometer.

The liquids used in the calibration of this instrument were the same as used for the capillary type. The revolving cup was adjusted to a speed of 56.4 r. p. m. and the larger disk bob and wire No. 32 were used in all determinations. The temperature of 100 cc. of the liquid to be measured was adjusted in the cup after first bringing it near to that temperature at which a reading was to be taken. The conversion curve in Fig. 7 shows that the degrees MacMichael deflection is a straight-line function of the absolute viscosity for all values above approximately 2 centipoises. Readings below this point, as pointed out by Herschel, are affected by turbulence and centrifugal forces, which make the curve tend to curve slightly at the lower end. This is shown more apparent in Fig. 8, where the factor  $cp./^{\circ} M.$ <sup>12</sup> is plotted against centipoises.

Temperature	$^{\circ} M.$	Cp.	Conversion Factor
<i>60 Per cent Sucrose Solution</i>			
60	134	9.83	0.0733
55	148	11.87	0.0789
50	179	14.01	0.0783
45	209	17.18	0.0822
40	248	21.28	0.0858
<i>40 Per cent Sucrose Solution</i>			
60	41.0	1.98	0.0483
55	43.5	2.22	0.0510
50	46.5	2.50	0.0538
45	49.5	2.85	0.0576
40	53.0	3.25	0.0613
35	59.0	3.76	0.0637
30	64.5	4.38	0.0680
25	75.0	5.19	0.0692
20	88.0	6.20	0.0705
15	103.5	7.47	0.0722
<i>Distilled Water</i>			
60	18.0	0.47	0.0261
45	20.5	0.60	0.0292
30	23.5	0.80	0.0341
<i>Medicinal Paraffin Oil</i>			
60	83	5.87	0.0707
45	118	8.96	0.0759
30	185	15.15	0.0819

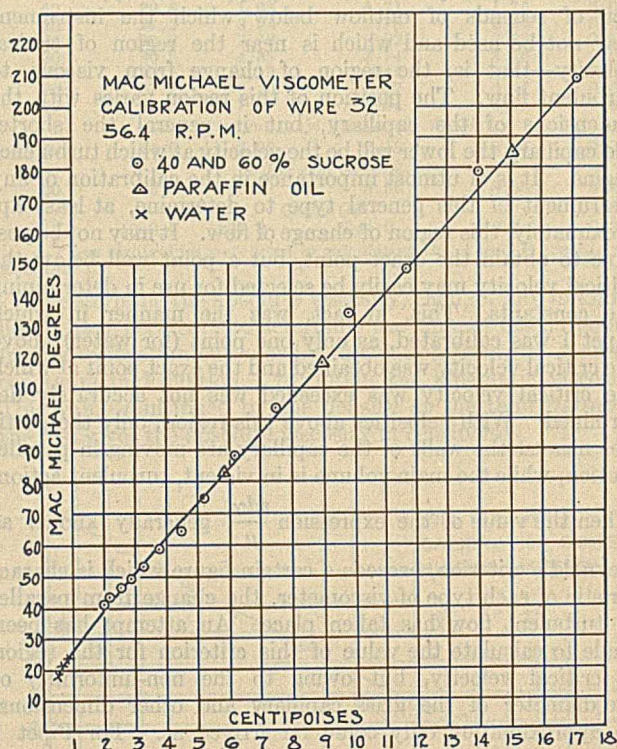


FIG. 7

In order to obtain comparative data on the MacMichael instrument and the capillary type pipet, portions of the

<sup>12</sup>  $^{\circ} M.$  = degrees MacMichael.

<sup>7</sup> THIS JOURNAL, 6, 233 (1914); "Fluidity and Plasticity," 1922, p. 316.

<sup>8</sup> Chem. Met. Eng., 23, 61, 197 (1920).

<sup>9</sup> THIS JOURNAL, 7, 961 (1915).

<sup>10</sup> Ibid., 12, 282 (1920); J. Optical Soc. Am., 7, 335 (1923).

<sup>11</sup> J. Am. Soc. Mech. Eng., 38, 626, 1002 (1916).

same solutions (in duplicate) of three glues were run on two pipets and in the MacMichael viscometer. The calibration curves for each were then used to calculate the absolute viscosity. The data obtained are given in Table V.

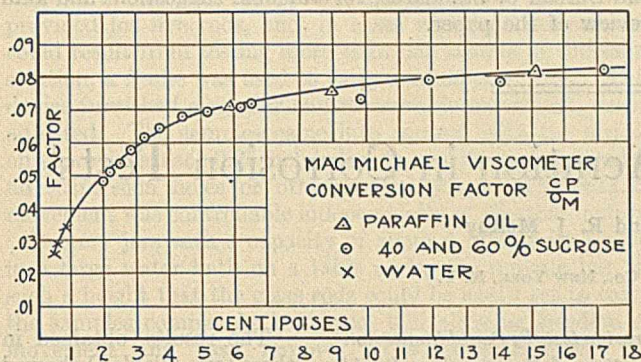


FIG. 8

TABLE V—COMPARATIVE VISCOSITIES BY MACMICHAEL VISCOMETER AND PIPETS 1 AND 2

Glue No.	MacMichael		Pipet 1		Pipet 2	
	° M.	Cp.	Sec.	Cp.	Sec.	Cp.
1	148	11.7	55.8	10.15	61.2	10.38
	146	11.5	56.2	10.19	61.2	10.38
	Av.	11.6	Av.	10.17	Av.	10.38
2	107	8.0	44.0	7.52	45.5	7.39
	105	7.8	43.2	7.34	45.8	7.24
	Av.	7.9	Av.	7.43	Av.	7.32
3	162	12.9	64.2	11.95	70.0	12.11
	163	13.1	65.0	12.11	70.4	12.19
	Av.	13.0	Av.	12.03	Av.	12.15

It will be noted in Table V that, while the two pipets check one another very closely, they do not give the same absolute viscosity as the MacMichael instrument. Attention is called to this discrepancy because it brings up a question which is of special interest. Is the viscosity of a colloidal solution dependent on the type of instrument used? Although it may be true that plastic substances like glues at lower temperatures have no constant viscosities, dilute glue solutions such as those used in this work and at a temperature of 60° C. are decidedly fluid substances, and when their previous histories (as in the foregoing cases) are carefully controlled, their apparent viscosities in absolute units appear to vary with the type of instrument used. The discrepancy increases with the grade—that is, with the viscosity. Whether it is due to a breaking down of the colloidal aggregate in passing through the small capillary of a pipet, causing a lower viscosity, or to the fact that a difference in the rate of shear affects the apparent viscosity of colloidal solutions or to a combination of the two, is not definitely known. With the MacMichael instrument the velocity of the solution at any point does not equal the velocity in the capillary, and therefore there is little tendency to damage the colloidal structure with this type. Excessive agitation has been shown to contribute largely to the lowering of the viscosity of glue solutions. In fact, when the operation of running them through a capillary is repeated on the same solution, a lower viscosity is usually observed. On the other hand, the effect of difference in the rate of flow has been observed only on glue solutions of 12.5 per cent concentration at 60° C., where an increase of about 27 per cent in velocity did not appreciably affect the viscosity recorded. However, the absolute viscosities recorded on the pipets for true solutions such as sucrose and glycerol check very closely with those recorded on the MacMichael instrument.

#### DISCUSSION OF CALIBRATING SOLUTIONS

For the calibration of commercial viscometers in absolute units, several liquids and solutions are available whose

viscosities are accurately known. Glycerol and sugar solutions have been studied and viscosities which agree very closely have been reported in publications of the Bureau of Standards.<sup>13</sup> With the equipment available in the present commercial laboratory, sucrose solutions containing 20, 40, and 60 per cent sucrose are probably useful only between 10° and 60° C., which gives a viscosity range between 0.81 and 109.8 centipoises. These solutions are readily prepared and standardized either by the density method or by means of the polariscope. The higher concentrations, however, vary in viscosity quite rapidly with a change in temperature, and therefore should be used with due consideration of the limits of error involved. This is the case with glycerol solutions, and to a greater extent. Here the viscosity changes very rapidly above a 55 per cent concentration.

The absolute viscosities of alcohol solutions are also available, and these are especially suitable for calibration purposes on low viscosities. Although alcohol solutions above ordinary temperatures are quite volatile, this fact is offset by the fact that their viscosities change only very slowly with a change in concentration. For the pipet calibrations mentioned above, as has been indicated, a 25 per cent solution of glycerol was used to fix the position of the calibration curve at its lower end, and a highly purified medicinal paraffin oil, the viscosity of which was determined by the Bureau of Standards by request, to fix the upper end of the curve. It will be noted from Table II that the only determination made above this point—namely, that of castor oil at 40° C.

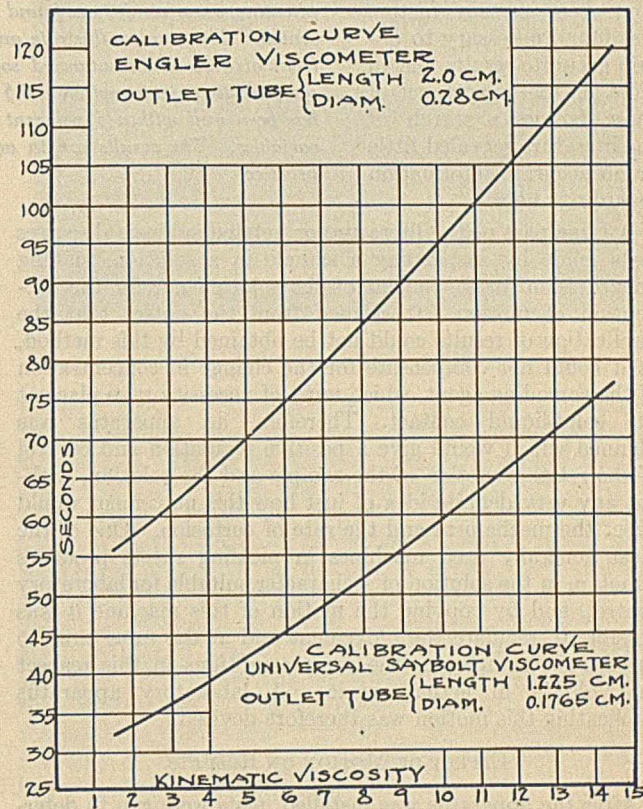


FIG. 9

—checks remarkably well with the value determined by Kahlbaum and Räber.<sup>14</sup> In general, nonvolatile oils are recommended for calibrating purposes at comparatively high viscosities. The absolute viscosities, when unknown, may be determined by sending about 200 cc. to the Bureau of Stand-

<sup>13</sup> *Bur. Standards, Sci. Paper 298* (1917).

<sup>14</sup> For discussion of viscosities of various castor oils, see *Bur. Standards, Sci. Paper 112*, 24 (1919).

ards or by an accurate determination on a long tube, calibrated viscometer.

#### ACKNOWLEDGMENT

The writer wishes to express his indebtedness to J. R. Powell, chief chemist of the Armour Glue Works Laboratory,

under whose supervision this investigation was carried out, for his many helpful suggestions and coöperation; to Robert H. Bogue, of Lafayette College, for his aid in the calibration of the MacMichael instrument, and to W. H. Herschel, of the Bureau of Standards, for valuable suggestions and kind review of the paper.

## The Control of Motion and Aeration in Corrosion Tests<sup>1</sup>

By J. F. Thompson and R. J. McKay

THE INTERNATIONAL NICKEL CO., NEW YORK, N. Y.

**A**CID corrosion tests of several "acid-resisting" metals were undertaken at the Mellon Institute of Industrial Research during 1920 to determine the causes of irregularities in the length of service obtained from Monel metal apparatus used for pickling steel sheets. As the tests progressed the control of certain factors was found necessary to obtain accurate results, but in spite of the importance of these factors a search of the literature revealed little or no accurate information regarding them.

A large part of the literature on related subjects discusses tests made by suspending a sample in a solution, making no provision for movement of the solution nor for the prevention of motion. It seemed from the outset that the duplication of results could not be obtained by this method, as it could not compensate for the change in concentration of the corroding agent, which must of necessity take place at the solid-liquid contact. Therefore, an apparatus was planned which would give a positive regulation and control of the relative motion of the sample and the solution, without any very definite idea of just how this movement would affect the mechanism and the rate of corrosion. One of the most generally used machines in pickling sheets produces a motion in the solution of a character suitable for laboratory control, and by copying the motion of this machine it was possible to regulate the movement and at the same time to subject the samples to the same conditions in this respect that obtain in actual service. A laboratory apparatus duplicating this motion was therefore devised.

#### EFFECT OF MOTION ON RESULTS

After the apparatus was installed, tests were run to determine the difference in the effect of motion or quiet, both from the standpoint of absolute corrosion rate and of reproducibility of results. The quiet and the moving<sup>2</sup> tests were made in all respects under the same conditions, except that in the quiet tests the drive motor of the moving mechanism was shut off.

<sup>1</sup> Received July 7, 1923.

<sup>2</sup> The terms "quiet" and "moving" are used in preference to "static" and "dynamic," favored by other writers, because the latter properly are used in reference to forces rather than to materials.

*Exact results can be obtained in corrosion tests by liquid immersion when quantitative control of the aeration of the corroding liquid and the motion of the corroding liquid relative to the corroded solid is maintained. Tests made to predict the practical service of factory equipment will be in error unless these important factors are duplicated, or accurately corrected for. Control is more difficult in quiet than in moving tests.<sup>2</sup>*

*The mechanism by which variation in aeration and rate of motion affects the corrosion rate is discussed. A test method of control sufficiently accurate to reproduce results within about 5 per cent is given. Also, results obtained in connection with a series of 2000 tests on acid-resisting metals in 2 to 10 per cent sulfuric acid, duplicating some conditions found in pickling steel sheets, are presented. The results illustrate an increase in rate of 500 per cent from air-free to air-saturated solution and of 600 per cent from comparative quiet to motion at 0.5 foot per second, but the agreement has been well within 5 per cent with quantitative control of these variables. The results are in accord with experience in pickling practice.*

The results obtained in these tests (Table I) showed such a surprising increase in the rate of corrosion and in the accuracy of results at even low velocities over the rate and accuracy obtained in quiet tests, that the plan of making quiet tests was discarded as useless. They could not furnish a prediction of practical results, nor were they accurate enough for any conclusions.

No increase in the rate was apparent between 0.25 and 0.5 foot per second. The percentage experimental error here is less than was usually obtained, but the usual effect of a much larger error in quiet than in moving tests is found. Of all tests made the average variation was 4.5 per cent for moving tests and 20 per cent for quiet tests.

TABLE I  
Air saturation about 15 per cent. Temperature 60° C.  
6 per cent sulfuric acid

Motion Rate Ft./Sec.	Corrosion Rate—Mg./Sq. Dm./Day—				Average Variations <sup>a</sup> Per cent
	Sample 2649	Sample 2661	Sample 2664	Average	
0.0	26	23	22	24	7
0.125	141	138	139	139	0.7
0.50	140	130	135	135	2.3

<sup>a</sup> Calculated by averaging the percentage variations of single tests from their average. This was found to be a useful measure of accuracy.

As the tests had for their purpose the study of corrosion of metals in the pickling of steel, they were made under conditions as nearly as possible duplicating those of actual pickling practice. The temperatures used ranged from 60° to 90° C., and the concentrations of acid from 2 to 10 per cent of sulfuric acid by weight.

#### APPARATUS FOR MOTION CONTROL

The movement of the samples relative to the solution was accomplished by the apparatus shown in Fig. 1. Virtual, harmonic, vertical motion was transmitted to a horizontal bar from an electric motor through a belt drive with cone pulleys, worm reducing gear, chain and cone sprockets, and adjustable crank. The motor was 0.5 horse power, 1700 revolutions per minute. The length of vertical stroke of the bar was adjustable in the yoke from a minimum of 0.5 inch to a maximum of 4 inches. The rate of stroke could be adjusted from 3 to 100 revolutions per minute. These adjust-

ments enabled a variation in the rate of movement of the sample through the solution from 3 to 800 inches per second.

Glass rods, bent in such a shape as to carry the sample with contact at only two places, passed through holes in the bar and were fastened rigidly by thumbscrews. Holes were provided for five rods, and, in cases where no inaccuracies could result from testing more than one sample in the same solution, a frame was used to carry a number of rods. This device furnished a regular and measurable movement, easily adjusted. The samples came into contact with the rod at only two lines, each 0.25 inch in length, and the sample needed no suspension holes or other special shape. The rate of movement was controllable independently of all other factors.

Battery jars with a capacity of about 4 liters were placed in a large water bath on a table under the moving bar, at such a height that the glass rods could be easily set to carry the samples completely immersed, still allowing freedom of movement and easy removal. The table carrying the samples rested on the floor, independent of the frame which carried the motor and other moving parts, so that there would be no vibration to disturb the contact film.

The fact that the motion was noncontinuous was considered a disadvantage, because there was a complete stop and also a maximum rate 50 per cent higher than the average. However, it was considered more satisfactory than a continuous rotation, because the swirling produced by rotation would make the actual velocity past the surface harder to determine. A continuous-flow apparatus to handle the solutions in question at known speeds, possible of regulation within wide limits, was considered too expensive; but, in view of the results obtained, it seems that such an apparatus would pay for itself in results of general value.

#### RESULTS WITHOUT CONTROL OF AERATION

After the apparatus was operating, results were obtained for a time which checked each other closely. Then unaccountable variations began to appear. Results varied as much as 20 per cent from one day to another, for no apparent reason. Finally, it was noticed that when the laboratory windows were left open in windy weather and there was an appreciable draft of air through the room, results were invariably high. The only obvious way in which this breeze could affect the tests was in blowing the steam away as it arose from the jars and thus coming in contact to a variable extent with the surface of the solutions. No reference could be found in the literature to differences in corrosion rate with an air contact in acid solutions of such a strength, but a consideration of the chemical reactions involved showed that a considerable effect might be expected. Therefore, the following test was devised to check the point:

Several samples of the same alloy were tested in the same solution, placed at different distances below the surface, while especial precautions were taken to keep the solutions quiet. The results were obtained in two typical tests. The distance from the surface as given is the center of the line in which the samples moved. The alloy used was Monel metal and the temperature and concentrations were the same as in Table I.

Distance from Surface Inches	Test 1	Test 2
	Mg./Sq. Dm./Day	Mg./Sq. Dm./Day
0.75	193	152
2.00	173	140
3.25	157	127

If the air contact with the surface affects the rate of corrosion, it would be expected that the samples near the surface would corrode at a more rapid rate than those at the lower levels. That this actually happens is shown with surprising definiteness by the results. The difference between the

results of Test 1 and Test 2 is typical of the variations that were being obtained at this stage of the research, but the effect of the greater supply of air near the surface is shown in both.

It was then suggested that if the air had such an important effect a convincing qualitative proof would be to direct a small stream of air against a plane surface of metal and thus

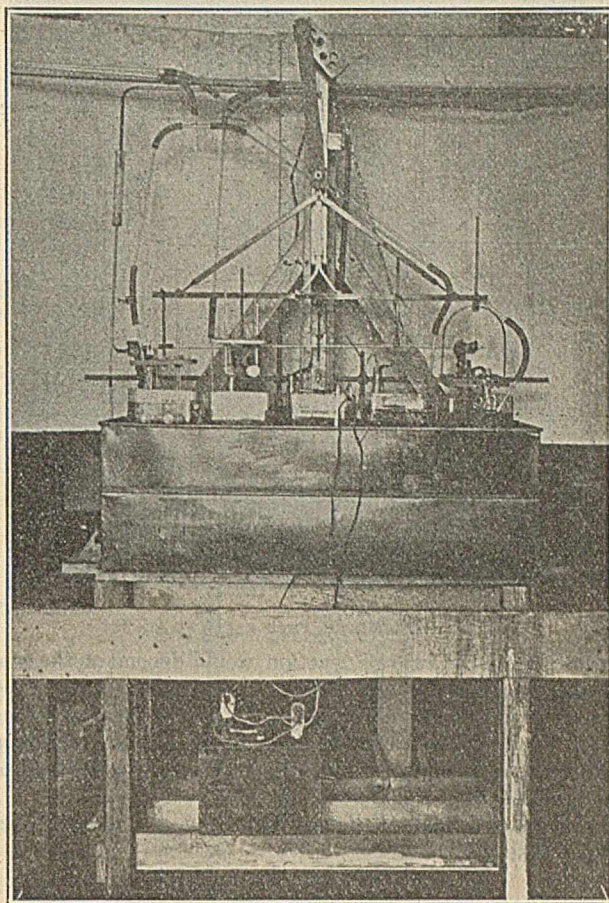
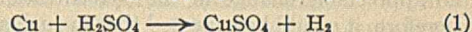


FIG. 1—FRONT VIEW OF THE APPARATUS

possibly produce an indentation at the point of contact. This experiment was tried by connecting the laboratory air line to a water-bottle delivery tube, so arranged under a 6 per cent acid solution that the stream of air was forced at right angles against the sample. The result was that 0.25-inch plate samples of several acid-resisting metals were completely perforated by the air jet before there was any appreciable thinning in the immediate neighborhood of the holes. Photographs of some representative samples are given in Figs. 2 and 3. These results were interesting in that they offered new enlightenment as to the mechanism of the corrosion and they furnished an explanation of certain of the practical phenomena. However, they demonstrated the necessity of control of the air content of the solution, which introduced new experimental difficulties.

#### NECESSITY OF AERATION CONTROL

The resistance of so-called "acid-resisting" metals to acid corrosion is due largely to the fact that they do not replace hydrogen in acids. Taking copper, for example, the reaction



will not proceed in the direction indicated. Consideration of the heats of reaction indicates that the reaction



will have a greater tendency to take place—in fact, it is exothermic, whereas Equation 1 is endothermic. The evident products of corrosion of copper by sulfuric acid are copper sulfate and water, and it is therefore probable that the reaction proceeds according to Equation 2. Therefore, it would be

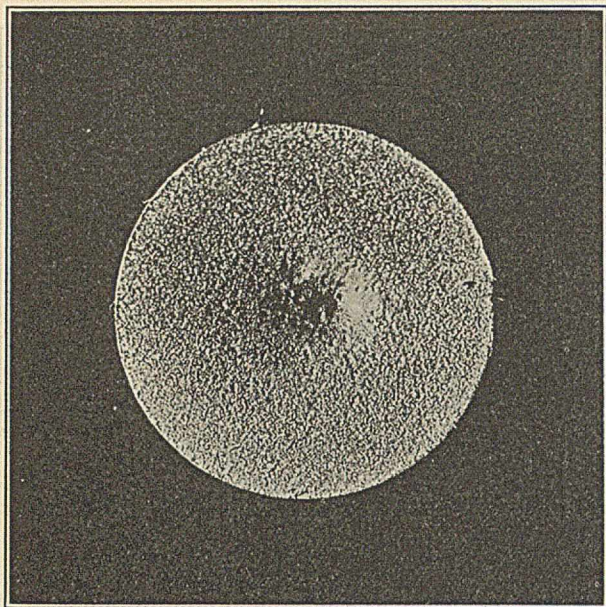
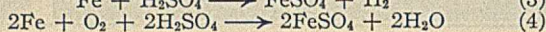
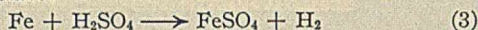


FIG. 2—MONEL METAL PERFORATED BY AIR JET

expected that the rate of reaction would depend on the concentration of Cu, O<sub>2</sub>, and H<sub>2</sub>SO<sub>4</sub>. In other words, dissolved oxygen should be as active in producing corrosion as a strong acid. Copper is here used as an example, but the reasoning will apply to any metal which will not directly replace hydrogen in acids.

For metals which will replace hydrogen, the following reactions take place:



As above, it would be expected that the reaction velocity would be increased by the presence of oxygen, but in this case both reactions are exothermic and the metal is corroded with considerable speed in both cases. The results given below are in agreement with this reasoning, as shown by the smaller effect of aeration in accelerating the corrosion of iron than of metals of low solution pressure. (Table V)

According to Seidell,<sup>3</sup> the solubility of oxygen from air in water at 25° C. is 0.0075 gram per liter, or about 0.00094 normal. In the present tests the concentrations of acid were from 2 to 10 per cent, or 0.5 to 2.0 normal. The concentration of acid is thus from 500 to 2000 times as great as that of oxygen. At 80° C. this ratio would probably be increased to a maximum of 10,000.

Thus, at the normal corrosion rate for copper in 2 to 10 per cent sulfuric acid, 1000 mg. per sq. dm. per day, a sample of area of 0.5 sq. dm. (an ordinary sheet sample 2 inches square) would exhaust the air from a 200-cc. corroding solution, according to Equation 1, in about 6 minutes, if the corrosion proceeded at the maximum rate. The concentration would be decreased 16 per cent in 1 minute and the rate of corrosion diminished accordingly. This is accompanied by no appreciable change in the concentration of the acid.

Therefore, it would be expected that in such a corrosion the rate would depend very much more on the concentration of air in solution than on the concentration of acid. This has been found to be true in the experiments of the authors.

<sup>3</sup> "Solubilities of Organic and Inorganic Materials," 1917.

The oxygen necessary for these reactions may, of course, be furnished by an oxidizing agent, if one is present, or by catalysts. These catalysts may be compounds, such as iron sulfates, which are oxidized readily by oxygen and reduced by metal, or finely divided or colloidal material carrying absorbed oxygen, or, in special cases, a combination of the two, as with the hydrates of iron.<sup>4</sup>

#### INTERDEPENDENCE OF MOTION AND AERATION

Since the reaction presumably only takes place at the surface of the metal, there is another condition to consider. Instead of the rate of reaction being determined by the concentration in the body of the solution, it is determined by the concentration in actual contact with the surface. As has been seen, the material whose contact must be considered is not the acid but dissolved oxygen. Therefore, a change in the supply of oxygen to this surface determines a change in the rate of motion of the solution and the rate of supply of oxygen to it. Thus, the rate of motion of the solution is of importance in supplying oxygen to the sample, and, within certain limits, the concentration in the contact film will vary with the motion and the rate of corrosion will increase with increase in motion.

Unless there is some continuous motion of the solution, the corrosion products will be unevenly distributed, owing to slight movements of the corroding liquid, and this will produce differences in the concentration of the corroding medium. The differences in concentration will set up quasi-concentration cells<sup>5</sup> which accelerate corrosion at one point and inhibit it in others. Therefore, the corrosion is uneven and such tests do not give duplicate results. A controlled moderate agitation of unvarying speed will largely prevent these effects and enable the reproduction of results. The agitated test is the more practical, because in most service cases of corrosion of acid-resisting metals the corroding medium is in movement.

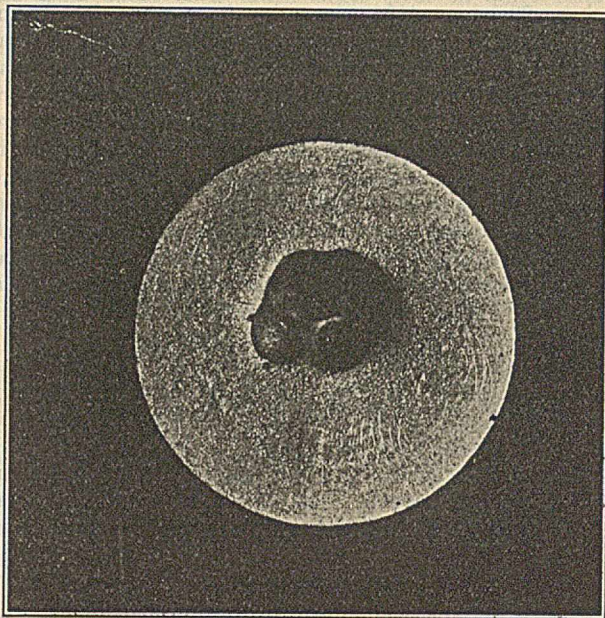


FIG. 3—ALUMINIUM BRONZE PERFORATED BY AIR JET

#### APPARATUS FOR AERATION CONTROL

In order to produce a known concentration of dissolved oxygen in the corroding solutions, the apparatus shown in

<sup>4</sup> Friend, *Trans. Am. Electrochem. Soc.*, **40**, 1 (1922).

<sup>5</sup> McKay, *Ibid.*, **41**, 201 (1922).



Fig. 4 was developed. An alundum crucible of medium fineness was fitted carefully with a rubber stopper. The stopper was cut thin to insure a perfect fit without breaking the crucible, and over it was placed a wooden disk held by strong, narrow rubber bands passing vertically around the crucible. The disk and stopper were bored to receive a glass tube connected with the pressure gas supply. This arrangement enabled the holding of sufficient air pressure within the crucible to produce a rapid emission of fine bubbles.

In use the stopper was so fitted on a bent glass tube as to lie in the bottom of the battery jar under an inverted glass funnel held on a glass standard. The funnel collected all the bubbles from the crucible and delivered them near the surface of the solution, thus preventing actual contact between the bubbles and the samples. The solution flowed up through the funnel with the bubbles, giving sufficient circulation to assure saturation with gas, but without affecting appreciably the average rate of movement relative to the sample.

It was necessary, in making a test, to use great care that this saturation device was operating at full efficiency. A small crack in the crucible or leak at the stopper allowing an appreciable proportion of air to flow in large bubbles invariably caused low results. The saturated condition was usually indicated by the formation of secondary minute bubbles in the solution from time to time, and unless this happened the saturating apparatus was not considered efficient.

In tests with the solution saturated with air the surface of the liquid was in contact with the laboratory atmosphere. In all others a glass cover was placed over the battery jar and neutral or suitable gas or gas mixtures were used in the saturator. The glass cover was a rectangular plate bored to admit the air tube, siphon, and sample support. Vapor from the warm solution condensed on this cover, sealing any slight openings. Interstices were left sufficient to allow the gas to escape. On the moving sample support a glass tube was fastened with a rubber tube in such a manner that the top end was sealed and the lower end fitted in the hole in the cover so as to seal the opening with a water film and still move freely up and down and allow the necessary play sideways. Thus, by controlling the relative volumes of gas admitted to the saturator, the concentration of oxygen or any active gas could be controlled independent of all other factors.

With apparatus as now developed it was again found possible to duplicate results closely. Some typical results are given in Table III.

TABLE III—MONEL METAL

Test	Temperature °C.	Rate of motion, 0.25 foot per second		Average Variation Per cent
		Concentration H <sub>2</sub> SO <sub>4</sub> Per cent	Corrosion Rate Mg./Sq. Dm./Day	
<i>Methane used in saturator</i>				
1	82	6	43	
2	100	3	71	
<i>Nitrogen used in saturator</i>				
1	82	10	135	
2		6	152	
3		6	135	
4		2	127	5.3
		Av.	137	
<i>Air used in saturator</i>				
1	82	10	726	
2			686	
3			692	
4			701	1.7
		Av.	701	
1	82	4	652	
2			685	
3			675	
4			682	1.6
		Av.	674	
<i>No saturator. Air in contact with surface of the solution</i>				
1	60	6	107	
2			157	
3			164	
4			194	
5			200	24
		Av.	144	

The much better duplication of results where the saturator was used is of note. The tests without the saturator were made during the first part of the investigation before the importance of the factors in oxygen supply discussed above were realized. The comparatively large variation in these tests resulted in the development of the saturator.

TABLE IV—COLD DRAWN COPPER  
Rate of motion, 0.25 foot per second

Test	Temperature °C.	Concentrated H <sub>2</sub> SO <sub>4</sub> Per cent		Corrosion Rate Mg./Sq. Dm./Day
		<i>Methane used in saturator</i>		
1	82	6	64	
2	100	3	78	
<i>Air used in saturator</i>				
1	60	6	1070	
2	60	2	1110	

The results obtained by using a reducing gas in the saturator were always lower than those wherein nitrogen was used. It is believed that this was because the nitrogen (from commercial tanks) contained a trace of oxygen or a slight amount of air was carried to the solution by drip from the glass cover. With the reducing gas this effect would be minimized.

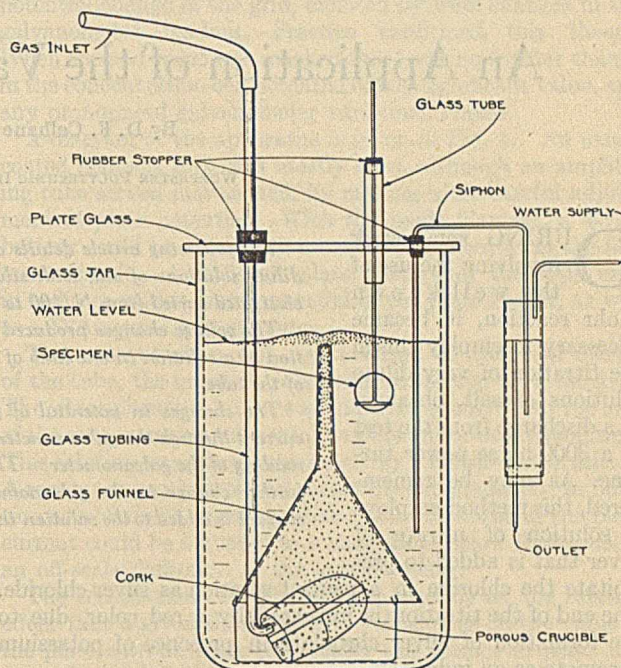


FIG. 4—AERATING APPARATUS

Tests made on about fifteen acid-resisting metals and alloys, with and without the presence of air, showed effects of the same order of magnitude in all cases.

According to the reasoning in this discussion, the effect of oxygen in the corrosion of steel should be less than in the corrosion of Monel metal. This inference was found to be true, and the relative effect on steel was found to be greater in the lower acid concentrations, which observation agrees with the interesting contemporary results of Whitman, Russell, Welling, and Cochrane.<sup>6</sup>

TABLE V—RATE OF SOLUTION OF COLD ROLLED STEEL

Sam- ple	Area Sq. Dm.	Weight G.	Loss Mg./Sq. Dm./Hr.	Ratio Loss Saturated with	Acceleration by Air Per cent
<i>Test 1: 82° C., 6 per cent H<sub>2</sub>SO<sub>4</sub>, 5 minutes</i>					
A	0.148	21.7491	0.6851	56	Air 0
B	0.143	18.1341	0.7492	63	Nitrogen
<i>Test 2: 82° C., 0.05 per cent H<sub>2</sub>SO<sub>4</sub>, 15 minutes</i>					
A	0.13	20.0935	0.0395	1.21	Air 22
B	0.12	17.0331	0.0296	0.99	Nitrogen
<i>Test 3: 82° C., 0.05 per cent H<sub>2</sub>SO<sub>4</sub>, 5 minutes</i>					
A	0.13	19.9352	0.0300	0.92	Nitrogen
B	0.12	17.1051	0.0341	1.14	Air 24

<sup>6</sup> THIS JOURNAL, 15, 672 (1923).

The many other factors which affect the rate of corrosion of metals will not be discussed, but the inadequacy of drawing conclusions from experiments in which agitation and aeration are incompletely controlled is to be emphasized.

The following notes mention briefly some of the other conditions existing throughout the tests. The duration of tests was usually 20 hours. In the absence of serious pitting, the loss in weight per unit surface per unit time was used as the measure of the corrosion rate.

Tests were repeated until the certainty of securing duplicate results was assured. The samples were of a standard size, a disk 1 inch in diameter and 0.25 inch thick. All surfaces were ground with zero emery before testing. Solutions were analyzed before and after all tests. A constant-level siphon furnished water to replace the rapid evaporation. The volume of solution was 3 liters. The sample was set on edge on two glass rods, making contact at only two places. Temperature was maintained by an electrically heated, thermostat-controlled bath covered with paraffin.

This investigation was begun for the purpose of studying certain practical problems and led to their solution before the effect of variation in rate of motion and of concentration of dissolved oxygen were fully determined. The pressure of other practical work has made it impossible to pursue the study with rapidity. It would be desirable to ascertain the effect of rate of motion over a greater range of speeds and the influence of air saturation; also to study other concentrations of dissolved oxygen. The data presented herein are sufficient to show that progress in corrosion study must be accomplished by thorough knowledge of these factors.

#### ACKNOWLEDGMENT

The authors take pleasure in acknowledging the valuable advice and assistance received from E. Ward Tillotson, assistant director of Mellon Institute of Industrial Research, where the research was conducted by the junior author.

## An Application of the Vacuum Tube to Chemistry<sup>1</sup>

By D. F. Calhane and R. E. Cushing

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**D**URING some work involving the use of the well-known Mohr reaction, it became necessary to employ this in the titration of very dilute solutions of salt, obtained as a discharge from the test of a 3000-horse power turbine. As may be remembered, this method employs a solution of nitrate of silver that is added to precipitate the chlorine in a neutral solution as silver chloride. The end of the titration is indicated by a red color, due to the formation of silver chromate in presence of potassium chromate as an indicator.

Under favorable conditions this is a very accurate titration. In the presence of any colored impurity in the water, or considerable precipitated silver chloride, the observance of the red color, or end point, is a matter of considerable difficulty. It then becomes necessary in some cases to remove the color of the water by chemical means.

It occurred to the writers that they might employ the three-electrode tube, so widely used in radio work, as a means of indicating the end point, without the necessity of relying on any color change.

It was found on consulting the literature that W. A. Noyes, Jr.,<sup>2</sup> had described a use of the three-electrode tube for the measurement of potential in an electrolytic cell for the deposition of iron. This avoided the shunting of an appreciable amount of current around the cell as would be the case when an ordinary voltmeter is used.

A brief description of the manner in which a three-electrode tube functions will make clearer the method of procedure in this work.

*The following article details a new method of accurately titrating dilute solutions of salt with silver nitrate. The concentrations investigated varied from N/100 to N/2500.*

*The voltage changes produced in a concentration cell during titration of a solution in one limb of it are impressed on the grid element of the tube.*

*The changes in potential of the grid vary the value of the plate current through the galvanometer, altering the magnitude of the scale reading of the galvanometer. The end of the titration is shown by no further change in the galvanometer deflection, when more titration reagent is added to the solution in one limb of the concentration cell.*

#### FUNCTION OF THREE-ELECTRODE TUBE

In the three-electrode tube a filament of fine wire, plain, or oxide-coated, is heated to a high temperature by a battery current. The high vacuum inside the tube allows negatively charged particles or electrons to be shot off from the hot filament. These

electrons are drawn over to a positively charged plate, the second element of the tube. The positive charge on the plate is produced by connecting it with the positive terminal of a second or plate battery. The negative terminal of this plate battery is connected with the negative side of the filament circuit. This provides a path for a current from the plate to the filament. If a galvanometer or milliammeter is connected into this circuit, a current will be indicated from the plate to the filament; the value of this current, within certain ranges, will be dependent on the magnitude of the filament current that conditions the temperature of the filament and the consequent flow of electrons.

If a third element, or grid, is placed between the filament and the plate, a means of controlling the magnitude of the plate current in two directions is available. If the grid is given a positive charge, it will attract negative electrons from the filament. A current will also be established in the grid circuit. If the grid is made negative, a reverse effect will be obtained and the plate current will be decreased for a given change in the potential of the grid. With a negative charge the grid, located between plate and filament, repels the negative electrons from the filament back to the filament, and thus reduces the value of the plate current in proportion to any change that may occur in the value of the negative potential of the grid. These changes in value of the plate current will be indicated by a galvanometer in the plate circuit. A means

<sup>1</sup> Received January 27, 1923.

<sup>2</sup> "Some Aspect of Electrolytic Iron," *Trans. Am. Electrochem. Soc.*, **40**, preprint (1921).

is thus obtained of noting any very small changes of potential that may occur in any system inserted in the grid circuit.

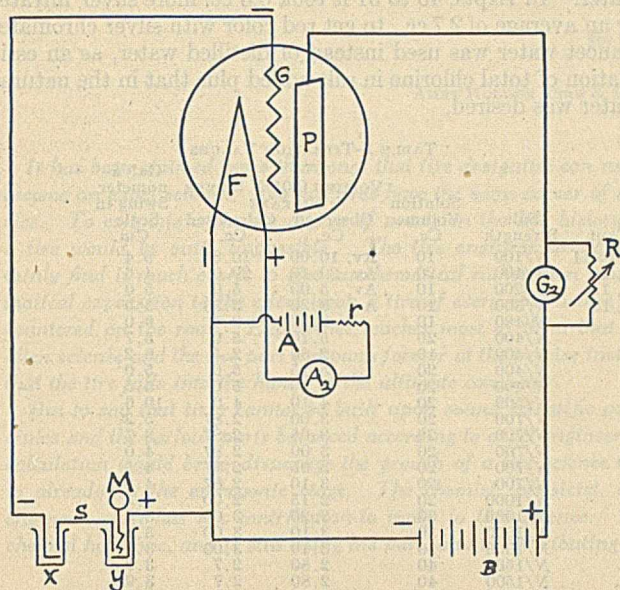


FIG. 1—APPARATUS FOR TITRATION OF SALT SOLUTIONS

F = Tube filament	A = Filament battery
G = Grid	r = Filament rheostat
P = Plate of tube	A <sub>2</sub> = Filament ammeter
G <sub>2</sub> = Galvanometer	x and y = Two limbs of concentration cell
R = Variable resistance box	S = Agar-filled siphon
B = Plate battery	M = Motor stirrer

(The solution to be titrated is in limb y)

About a year ago a conductivity cell was tried in the grid circuit. The idea was to titrate out the salt in the usual way, and rely on a change in resistance of the cell to alter the grid potential. This scheme proved fundamentally inoperative since no current flows in the grid circuit when the grid is negatively charged; therefore, a change in resistance of the titration cell would cause no perceptible voltage change on the grid.

The idea that a concentration cell connected in the grid circuit would function in the way desired was found to be correct. This forms the basis of this new method of titration.

#### PRINCIPLE OF CONCENTRATION CELL

With this device there are two electrodes dipping in solutions of different strength, each electrode and solution in a separate container. When these two single cells are connected by a conducting siphon, a battery is formed, which affords a feeble current from the more dilute solution to the more concentrated, thence through the external circuit back to the electrode in the more dilute solution. The current will flow as long as there is a difference in concentration between the two solutions. The energy that affords voltage to propel a current is seated in a change of osmotic pressure that continually goes on during the equalization of the concentrations. When the concentrations are completely equalized in the two parts of the cell, no further voltage changes, and consequently current flow, will occur.

#### APPLICATION TO SALT TITRATION

The writers were interested in making use of the change in potential of the electrode dipping in the salt solution of unknown strength. This concentration was to be continually altered by titrating out the chlorine of the salt with silver nitrate in the usual way. A concentration cell was made up of two small beakers, connected by a siphon of solidified agar, which contained *N*/10 potassium nitrate to give conductivity.

In the known limb of the cell was a silver wire dipping in *N*/10 potassium chromate saturated with silver chromate. There might also be used here a dilute solution of sodium nitrate saturated with silver chloride plus one or two drops *N*/100 silver nitrate. In the other cell or beaker was a silver wire dipping into the unknown salt solution whose strength was to be determined by titration with silver nitrate.

By connecting this cell in the grid circuit of the three-element tube so that a change in the negative potential of the grid would be produced as the titration proceeded, a means of determining the end point electrically would be provided by the indications of the galvanometer in the plate circuit.

To explain this more completely, as chlorine is precipitated by titration in one limb of the concentration cell, the electrode potential in that arm will increase, owing to removal of chlorine ions. This will cause an increase of the negative potential on the grid, which produces a reduction of the plate current in the tube, shown by a diminishing change in the galvanometer reading.

Very close to the end point, the chlorine will be removed relatively at the fastest rate, causing a rapid and marked potential change of the grid, denoted by wide changes in the galvanometer reading. Practice confirmed this theory. When the end point was reached there was no further change in the concentration cell potential of any significant value, and any pronounced galvanometer variations ceased.

A diagram of the apparatus is given in Fig. 1. An oxide-coated filament tube was mostly used, although an amplifying tube served just as well, by making more careful adjustment of plate potential. With the oxide filament, a 4-volt battery could be used, with a controlling rheostat in the filament circuit. A 22.5-volt plate battery of the type used in radio operation was connected in the plate circuit, as well as a D'Arsonval galvanometer.

The concentration cell was inserted in the grid circuit of the tube, the negative pole being connected with the grid. The silver nitrate solution was run from a buret into the arm of the concentration cell containing the unknown salt solution. This solution was stirred vigorously by a motor-driven stirrer. A resistance box was placed across the galvanometer, to function as a variable shunt, so that the initial value of the plate current could be adjusted to a magnitude below that causing an off-scale deflection of the galvanometer.

The sensitiveness of this method depends on the relative effect that a given change in grid voltage has on the value of the plate current, since the greater this change in plate current effected by the grid variation in voltage, the larger will be the galvanometer deflection.

#### AMPLIFYING FACTOR

These points may be more clearly expressed by considering what is known as the amplifying factor of a three-electrode tube, and the curve that expresses the relationship between plate current and grid voltage variations, for a constant plate voltage.

The amplifying factor equals plate volts change for a given plate current change divided by grid volts change for the same plate current change. This may be succinctly expressed by the expression

$$u = \frac{dI_p}{dE_g} \div \frac{dE_p}{dI_p}$$

As operated, there is a fixed plate voltage in the tube, with a resulting plate current for a fixed filament current, for any one condition. As the grid voltage changes owing to any external cause the plate current varies by a certain amount referable to the amplification factor. The factor for the tube used was about 5.

In order to have these plate current variations as great as possible for a minimum grid voltage change, the constant grid potential for any fixed condition of the system should lie on the steepest portion of the grid-voltage-plate-current curve of the electron tube. Such a set of curves for the tube used in this work is shown in Fig. 2. The plate voltage was 23.7 volts and the filament current 1.1 amperes. This gives a desirable grid voltage swing or variation from  $-1$  to  $+1$  volt, on the steep portion of the plate-current-grid-voltage curve.

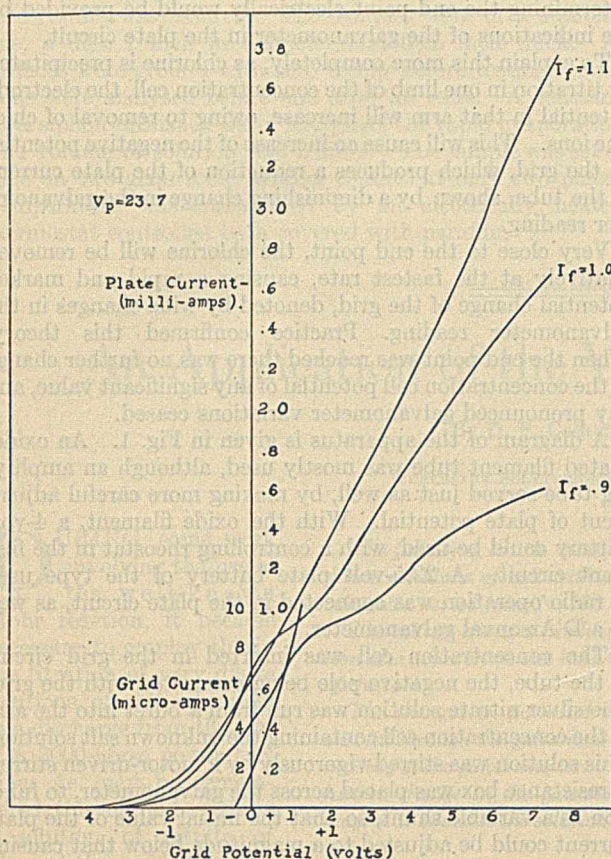


FIG. 2

## RESULTS

To show the working of this method, a tabulation of a typical set of results will be most convincing. A salt solution is titrated whose strength in salt is continually diminished. The amount of this solution is listed, and the variation of the galvanometer indicated. Solutions varying in strength from  $N/100$  to  $N/2500$  are listed. This means a variation of the salt concentration from 5.85 mg. in 10 cc. of 0.01 normality to 0.936 mg. of salt present in 40 cc. of 0.0004 normality. In all titrations the galvanometer makes the most of the swing noted on the addition of last three or four drops of the silver nitrate added to effect the end point. This is in accordance with the theory of the concentration cell.

Ordinary colors in natural waters give no interference with this method. The end point could be more accurately attained on known solutions than with the potassium chromate indicator. This removes the personal equation in the observance of color.

In Expt. 21 the salt solution was colored with methyl blue. In Expt. 23 the end point with potassium chromate was distinguishable only at 5.8 cc.; in Expt. 24, 4.7 cc.; Expt. 37, 4 cc.; and Expt. 39, 3.6 by the same method.

The values in Column 5 are calculated for pure salt in distilled water. Where faucet water was used for volumes

of 30 to 40 cc. salt solution titrated, these values should be increased by 0.3 to 0.4 cc. to account for chlorine in natural water. In Expts. 43 to 51 it took 0.3 cc. more silver nitrate, or an average of 2.7 cc., to get red color with silver chromate. Faucet water was used instead of distilled water, as an estimation of total chlorine in salt added plus that in the natural water was desired.

TABLE I—TITRATION VALUES

Expt.	Salt Strength	Solution Volume Cc.	VOLUME 0.01 N SILVER NITRATE		Galvanometer Swing in Scale Cm.
			Observed Cc.	Calculated Cc.	
1 to 11	$N/100$	10	Av. 10.00	10.0	5.4
12, 13	$N/100$	20	Av. 20.10	20.0	4.6
14, 15	$N/200$	10	Av. 5.00	5.0	5.0
16, 18	$N/300$	10	Av. 3.20	3.33	5.0
19	$N/400$	10	2.60	2.5	6.0
20	$N/400$	20	5.10	5.0	5.7
21	$N/400$	10	2.60	2.5	6.2
22	$N/400$	20	5.15	5.0	5.0
23	$N/400$	20	5.10	5.0	5.5
24	$N/500$	20	4.10	4.0	10.6
25	$N/700$	20	3.00	2.87	5.2
27	$N/700$	20	3.05	2.87	3.7
28	$N/700$	20	3.00	2.87	4.0
29	$N/700$	20	3.05	2.87	4.5
30	$N/700$	20	3.10	2.87	4.3
33	$N/1000$	20	2.15	2.00	4.5
36	$N/1000$	30	3.20	3.00	3.6
37	$N/1000$	30	3.10	3.00	3.6
38	$N/1000$	30	3.10	3.00	3.4
39	$N/1500$	40	2.80	2.7	3.9
40	$N/1500$	40	2.80	2.7	3.9
41	$N/1500$	40	2.90	2.7	3.7
42	$N/1500$	40	2.80	2.7	3.8
43 to 51	$N/2000$	40	Av. 2.10	2.0	3.2 (Av. 7 expts.)
52	$N/2500$	40	1.70	1.6	3.0
53	$N/2500$	40	1.75	1.6	3.0
54	$N/2500$	40	1.70	1.6	3.0

With a  $N/2500$  salt solution, 1 cc. of  $N/1000$  salt solution is equivalent to 25 cc. of  $N/2500$  strength. So 40 cc. of  $N/2500$  are equivalent to 1.6 cc. of the  $N/100$  strength.

The faucet water used to make up the solutions required between 0.3 and 0.4 cc.  $N/100$  silver nitrate, and gave a visible turbidity of silver chloride. The agreement is thus sure to be close enough to establish the accuracy of the method.

Even with 40 cc. of tap water, the galvanometer gave a readable deflection of 0.7 cm., which goes to show the extreme sensibility of the method. The galvanometer variation from Expts. 36 to 54— $N/1000$  to  $N/2500$  for average of 40 cc.—is only about 1-cm. scale. The decrease in sensibility of the galvanometer is very slow as dilution proceeds.

Work along these lines will be pursued in this laboratory.

## Use of Glue in Paper Coating

The Bureau of Standards is conducting some experiments on the use of glue in coating paper. During the past month nine runs have been made on the experimental coating machine, using two makes of bone glue for eight of the runs and a French casein glue for one. The clay used for all runs was Lee Moor, a good grade of English coating clay. The results indicate that the water resistance of glue-bound coating containing chrome alum compares favorably with that of casein-bound paper containing no formaldehyde. It is believed that the degree of waterproofness will prove sufficient for most of the papers used for halftone printing. Difficulties have been experienced in obtaining a uniform coating, because of variation of the fluidity of the coating mixture and mechanical defects in the machine, so that additional work will be necessary before paper suitable for printing test can be produced.

The sum of \$1500 has been placed at the disposal of the College of Agriculture of the University of Wisconsin by the Sewerage Commission of the City of Milwaukee for the establishment of a fellowship to study the best methods of using activated sludge as a fertilizer. This material is prepared in large quantities as a by-product in the disposal of Milwaukee sewerage. O. J. Noer has been appointed to the fellowship, which will be under the jurisdiction of the soils department.

# Fabric Stresses in Pneumatic Tires<sup>1</sup>

By H. F. Schippel

AMES HOLDEN TIRE & RUBBER CO., LTD., KITCHENER, ONT.

It has been claimed more than once that tire designing can never become an exact science. No two tires have the same career of service. To estimate with any degree of precision the life history of a tire would be quite impossible. The tire engineer would certainly find it much easier to give anathematical rather than mathematical expression to the effect upon a tire of every obstruction encountered on the road. Experience teaches most of them that too often science and the tire part company forever at the precise instant that the tire falls into the hands of the ultimate consumer.

But to say that tires cannot be built upon sound scientific principles and the various parts balanced according to exact engineering calculation would be to disparage the growth of a tire science that is already in the embryonic stage. The chemist, physicist, and engineer, each has his contribution to make to this science. The chemist has done, and is still doing his part, and is contributing his

work to the chemical literature. But of the intricate work of the physicist and the engineer we hear deplorably little. Their work is embodied in the finished tire that leaves the factory. The many indications of astute scientific application in these tires attest the progress that is being made. Whether the result is achieved by the process of experiment or by mathematical calculation is not often clear. But there is no doubt that the latter method would often shorten the toil and expense of the former, by eliminating unnecessary and condensing the necessary experiment, and thereby accelerating the conclusion.

It is with the foregoing thoughts in mind that the writer presents this mathematical analysis of fabric stresses in pneumatic tire carcasses, and while it covers but a small part of the field of tire design, it is hoped that opportunity will occur in the future to offer similar analyses of other complex problems that confront the tire designer.

THE definite commensurable stresses to which the fabric of a tire carcass is subjected are the following, which will be called static or dynamic according as they occur when the car is at rest or in motion: Static—(1) stresses due to inflation pressure, (2) stresses due to deflection under load; Dynamic—(3) traction and braking stresses, (4) centrifugal stresses.

There are, in addition, those indeterminate stresses due to road shocks. Their magnitude cannot easily be calculated, and the tire must be more or less safeguarded against them by an adequate factor of safety. But a liberal factor of safety can never successfully conceal an ignorance of the fundamentals of tire design. The reason is simple. The tire may successfully withstand the severe shocks which usually occur only a relatively small number of times, but there is a great danger that it may eventually be destroyed by the insidious action of an oft-repeated minor stress caused through faulty design.

## STRESSES DUE TO INFLATION PRESSURE

A tire carcass is essentially a cylindrical vessel containing air under pressure. There are two principal stresses in an inflated hollow cylinder made of thin homogeneous material—the transverse stress, and the longitudinal stress.

Let  $P$  = internal air pressure

$D_T$  = internal diameter

Then the transverse stress  $S_T$ ,<sup>2</sup> per inch of axial length

$$= \frac{PD_T}{2} \quad (1)$$

and the longitudinal stress  $S_L$  per inch of transverse periphery

$$= \frac{PD_T}{4} \quad (2)$$

The transverse is the major stress, and is double the longitudinal stress.

But in the tire these simple stress equations are complicated by five considerations: (1) elliptical transverse section of the inflated tire, (2) inflation stress in the tube, (3) toroidal shape of the tire, (4) fibrous grain of the carcass, and (5) carcass thickness. All these factors vary with each different

size of tire, and the true value of fabric stress can be obtained only by calculating the effect of each factor.

1—The cross-sectional shape of an inflated tire is usually elliptical, the major axis having a direction parallel to the axis about which the tire revolves. This ellipticity is a function of the principal diameter of the tire and of the angle at which the fabric threads lie in the carcass. Its effect is to decrease the transverse fabric stress in the same way that a flattening of the ideal hollow cylinder would diminish the transverse stress  $S_T$ . The effective diameter  $D_T$  of the cylinder for the purpose of transverse stress calculation becomes the minor axis of the elliptical section.

2—The actual pressure per unit area acting upon the inside of the carcass is less than the inflation pressure by the amount of pressure necessary to inflate the tube to fit the inner walls of the carcass.

Let  $P_T$  = the pressure necessary to inflate the tube

Then the pressure acting upon the carcass =  $P - P_T$  (3)

The value of  $P_T$  may be approximated by testing a tube already manufactured, or may be derived mathematically as follows:

Let  $L_c$  = internal cross-sectional perimeter of the surface of the inflated tire against which the tube must bear

$L_T$  = cross-sectional perimeter of the outer surface of the noninflated tube

$t$  = tube thickness

$m$  = average elastic modulus of tube stock up to the strain of normal inflation

Then the strain per unit of transverse perimeter of tube

$$= \frac{L_c - L_T}{L_T}$$

and the stress per unit of circumferential length of tube

$$= mt \left( \frac{L_c - L_T}{L_T} \right)$$

and the tube inflation pressure  $P_T$

$$= \frac{2\pi}{L_c} mt \left( \frac{L_c - L_T}{L_T} \right)$$

$$= 2\pi mt \left( \frac{L_c - L_T}{L_c L_T} \right) \quad (\text{See appendix}) \quad (4)$$

3—The toroidal shape of the tire presents another complexity.

The longitudinal stress  $S_L$  remains unchanged (Equation 2),

<sup>1</sup> Received July 26, 1923.

<sup>2</sup> Burr, "Elasticity and Resistance of Materials of Engineering," 1915, p. 197.

but the transverse stress  $S_T$  becomes

$$\frac{D_T D_R (P - P_T)}{2(D_R + D_T)} \quad (5)$$

for the synclastic part of the tire under the center of the tread, where  $D_R$  = the principal diameter of tire to the sectional major axis, or in general

$$S_T = \frac{D_T D_R (P - P_T)}{2(D_R + 2H)} \quad (6)$$

for any point on the carcass distant  $H$  from the sectional major axis, positive in the direction of the tread, and negative in the direction of the bead.<sup>3</sup> This effect diminishes the fabric stresses toward the tread region.

4—The fibrous grain of the carcass has a most important bearing upon the fabric stress values. The tire carcass is made of bias-laid fabric, through which the transverse and longitudinal stresses transmit interfering components.

To obtain the component along the fabric threads at any point on the carcass of the transverse stress  $S_T$ , consider a unit length  $AC$  (Figs. 1 and 2) of the carcass parallel to the longitudinal axis. The force acting perpendicularly on this unit length  $AC$  is the transverse stress  $S_T$ .

Let  $F$  = the integral of the reacting force in the threads crossing  $AC$  in each direction, respectively

$\theta$  = the angle between the threads and the line  $AC$

$N$  = number of plies of square-woven fabric, or pairs of plies cord fabric; then

$$S_T = 2FN \sin \theta \quad (7)$$

$$\text{or } F = \frac{S_T}{2N \sin \theta}$$

Substituting the value of  $S_T$  from Equation 6

$$F = \frac{D_T D_R (P - P_T)}{4N(D_R + 2H) \sin \theta} \quad (8)$$

But the force  $F$  acts over a width of fabric  $CD$ , measured perpendicularly to the direction of the threads, so that the force  $F_1$  per unit width of fabric becomes

$$F_1 = F \frac{AC}{CD} = F \frac{AC}{AC \sin \theta} = \frac{F}{\sin \theta} = \frac{D_T D_R (P - P_T)}{4N(D_R + 2H) \sin^2 \theta} \quad (9)$$

It is now necessary to consider the distortion of the fabric to conform to the curvature of the carcass. When the fabric suffers an angular distortion, the number of threads per unit distance measured perpendicularly to their direction is increased or decreased according to the angle at which the fabric was originally cut, and the deformation received in building the carcass.

Let  $B$  = angle between cutting line and fabric selvage

Considering the distortion of a parallelogram, whose sides are parallel to the two thread directions, respectively,

Let the larger undistorted internal angle =  $2B$ , and the corresponding distorted angle =  $2\theta$

Then the ratio of the thread densities,

$$\frac{\text{Distorted density}}{\text{Original density}} = \frac{\sin 2(90 - B)}{\sin 2(90 - \theta)} = \frac{\sin 2B}{\sin 2\theta} \quad (10)$$

and the fabric stress per unit width of original fabric is the inverse of this ratio. Therefore, the stress  $F_1$  per unit original width of fabric

$$F_1 = \frac{(P - P_T) D_T D_R}{4N(D_R + 2H) \sin^2 \theta} \times \frac{\sin 2\theta}{\sin 2B} \quad (11)$$

This equation can be simplified for the purpose of calculating the stress in any specific instance by expressing the angle  $\theta$  in terms of the angle  $B$  and fabric stretch.

Let  $S$  = ratio of stretched to unstretched length of the fabric at the extreme ply diameter; then it can be proved that

$$\theta = \cos^{-1} \left\{ S \cos B \left( \frac{D_R + 2H}{D_R + D_T} \right) \right\} \quad (12)$$

(See appendix)

Equation 11 enables us to calculate the average value per ply of the component of transverse stress  $S_T$  acting along the direction of the fabric threads in the zone  $AC$ . This component  $F_1$  acts in such a way as to shorten the circumferential length of the tire and shrink it on the rim, thereby producing the characteristic elliptical cross-sectional shape of the tire, and relieving the bead of no inconsiderable amount of stress. It is to be noted that as the zone under consideration approaches the tread region of the tire,  $H$  increases and  $\theta$  decreases, so that the variations of these two coefficients produce opposite effects, but that due to the variation of fabric angle is by far the greater.

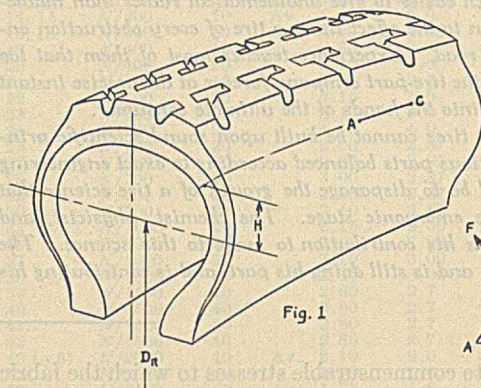


Fig. 1

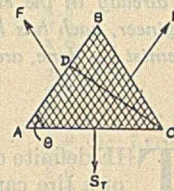


Fig. 2

It is interesting to observe the combined effect of the angle  $B$  and stretch  $S$ , as shown by the curves in Fig. 3A. These curves refer to the maximum fabric stress, which occurs on the inner ply underneath the center of the tread.

At this point  $D_T = 2H$ , so that  $\cos \theta = S \cos B$ .

One is impressed by the apparently large range of choice of fabric stress. Were inflation the sole consideration, one would naturally choose as low a value as would be consistent with high manufacturing efficiency. But consideration must also be given to other stresses to which the carcass is subjected, which are also a function of the bias angle and fabric stretch. These stresses will be determined later.

By a process similar to that by which Equation 9 was derived, and elaborating upon the simple Equation 2, it can be shown that the component  $F_2$  of the longitudinal stress  $S_L$  acting along the fabric threads is

$$F_2 = \frac{(P - P_T)}{8N} \sqrt{a D_T} \sec^2 \theta \frac{\sin 2\theta}{\sin 2B} \quad (13)$$

(See appendix)

where  $a$  = major axis of cross-sectional ellipse

The longitudinal component opposes the transverse component, and being the smaller force, its sole effect is to reduce the intensity of the contracting force of the tire on the rim. It does not reduce the fabric stress.

By equating the longitudinal to the transverse stress and solving for the angle  $\theta$ , it will be found that the fabric angle, for which there is no resultant contractive force of the tire on the rim, approximates very closely to the angle 54.7 degrees, which is the "angle of repose" for the ideal right circular cylindrical vessel. For this fabric angle the inflated carcass would have a circular, not an elliptical, cross section. On account of the toroidal shape of the tire, the fabric angle is not uniform, but varies from tread to bead, so that the average fabric angle should equal the "angle of repose."

5—In deriving the foregoing equations of ply stresses in a tire carcass, we have considered the tire as an ideally thin vessel, and the stresses equally divided among all the plies.

<sup>3</sup> Poynting and Thomson, "Textbook of Physics. Properties of Matter," 1909, p. 145.

A tire carcass, however, has a considerable thickness as compared with its other dimensions, and this thickness causes an unequal distribution of the inflation stress throughout the carcass.

Let  $E$  = cross-sectional ellipse perimeter at median line of noninflated carcass

$dE$  = increase of  $E$  due to inflation

$T$  = thickness of one square-woven ply, or of one pair of cord plies

Then, because all the plies are bound together by the rubber skim coats,

the transverse elongation of all plies =  $dE$

the unstrained length of first or

inner ply =  $E - \pi T(N-1)$

that of the second ply =  $E - \pi T(N-3)$

that of the third ply =  $E - \pi T(N-5)$

that of the Xth ply =  $E - \pi T[N - (2X-1)]$

Therefore, the strain per unit transverse length of first ply

$$= \frac{dE}{E - \pi T(N-1)} \quad (14)$$

that of the second ply

$$= \frac{dE}{E - \pi T(N-3)} \quad (15)$$

that of the Xth ply

$$= \frac{dE}{E - \pi T[N - (2X-1)]} \quad (16)$$

Let  $M$  = average elastic modulus of the fabric up to strain  $dE$

Then the transverse ply stress

=  $M$  · transverse ply strain

the transverse stress on the first ply

$$= \frac{M \cdot dE}{E - \pi T(N-1)} \quad (17)$$

that on the Xth ply =  $\frac{M \cdot dE}{E - \pi T[N - (2X-1)]}$  (18)

To obtain the fabric stress per unit width of fabric, it is only necessary to multiply the right-hand sides of these equations

by  $\frac{1}{2 \sin^2 \Theta} \times \frac{\sin 2\Theta}{\sin 2B}$  so that

fabric stress in the first ply

$$= \frac{M \cdot dE}{E - \pi T(N-1)} \times \frac{1}{2 \sin^2 \Theta} \times \frac{\sin 2\Theta}{\sin 2B} \quad (19)$$

and that in the Xth ply

$$= \frac{M \cdot dE}{E - \pi T[N - (2X-1)]} \times \frac{1}{2 \sin^2 \Theta} \times \frac{\sin 2\Theta}{\sin 2B} \quad (20)$$

For the small values of  $N$  such as occur in tires, the stress equations for the consecutive plies may be taken as an arithmetic series, having an average value of

$$\frac{M \cdot dE}{E} \times \frac{1}{2 \sin^2 \Theta} \times \frac{\sin 2\Theta}{\sin 2B} \quad (21)$$

Equating this to the average fabric stress as derived in Equation 11,

$$\frac{D_T D_R (P - P_T) \sin 2\Theta}{4N (D_R + 2H) \sin^2 \Theta \sin 2B} = \frac{M \cdot dE}{E} \times \frac{1}{2 \sin^2 \Theta}$$

and transposing

$$M \cdot dE = \frac{D_T D_R E (P - P_T)}{2N (D_R + 2H)} \quad (22)$$

Substituting this value of  $M \cdot dE$  in Equation 20, we obtain the general expression for fabric stress  $F_P$  in the Xth ply of

$$\frac{D_T D_R (P - P_T)}{2N (D_R + 2H)} \times \frac{E}{E - \pi T [N - (2X-1)]} \times \frac{1}{2 \sin^2 \Theta} \times \frac{\sin 2\Theta}{\sin 2B} \quad (23)$$

This is a complete expression for ply stress involving the five tire complexities of elliptical transverse section, tube inflation, toroidal shape, fibrous grain, and carcass thickness.

To check the accuracy of this stress equation, and to illustrate its application to a definite tire, let us calculate the internal bursting pressure of a 33 x 4 straight-side cord tire, and compare with the pressure obtained by actual test. The

point of maximum fabric stress occurs at the inner ply, underneath the center of the tread.

$P$  = 60 pounds per square inch = normal inflation pressure

$P_T$  = 4 pounds per square inch = pressure to inflate tube

$D_T$  = 3.92 inches = minor axis of cross-sectional ellipse at median line of normally inflated carcass

$D_R$  = 29.56 inches = principal diameter of tire, to major axis of inflated cross-sectional ellipse

$E$  = 11.7 inches = cross-sectional ellipse perimeter at median line of noninflated carcass

$N$  = 3 = number of pairs of cord plies

$H$  = 1.96 inch = distance from the sectional major axis of the point, on the carcass median line, at which the stress is to be calculated

$T$  = 0.090 inch = thickness of one pair of cord plies

$X$  = 1 = the number of the double ply for which the stress is to be calculated, counting outward from the inner pair of plies

$\Theta$  = 33.5 degrees = angle between the cords and a line parallel to the longitudinal tire axis

$B$  = 45 degrees = angle of bias cut

Then the maximum fabric stress  $F_P$  =

$$\frac{3.92 \times 29.56(60-4)}{2 \times 3(29.56 + 3.92)} \times \frac{11.7}{11.7 - 3.1416 \times 0.090(3-1)} \times \frac{2 \times 0.551^2}{1} \times \frac{0.920}{1.00}$$

$$= 32.3 \times 1.051 \times 1.649 \times 0.92$$

$$= 51.5 \text{ pounds per inch width}$$

The fabric strength per inch = 18.0 pounds per cord  $\times$  23 cords = 414 pounds

Therefore, bursting pressure =  $\frac{414}{51.5} \times 56 = 451$  pounds per square inch

A correction must here be made to allow for the increased fabric stretch from normal inflation to bursting inflation.

Fabric stretch at 60 pounds inflation = 6.3 per cent

Fabric stretch at failure = 18.0 per cent

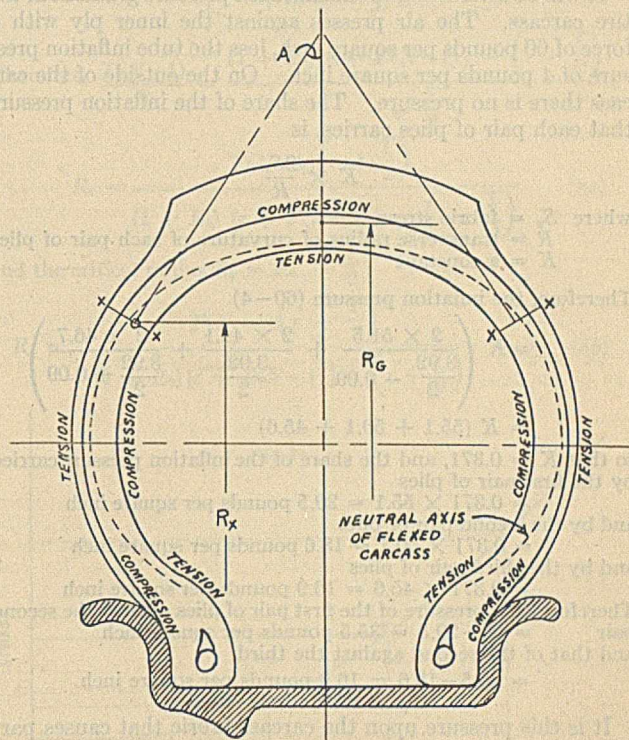


Fig. 3

This increased stretch increases the minor axis  $D_T$ , and reduces the bursting pressure.

True bursting pressure =  $451 \times \frac{1.063}{1.180} = 406$  pounds per square inch.

By actual hydraulic test, the bursting pressure was 388 pounds per square inch.

It may readily be calculated that the maximum fabric stress on the second pair of plies is 49.1 pounds per inch width, and on the third pair of plies, 46.7 pounds per inch width.

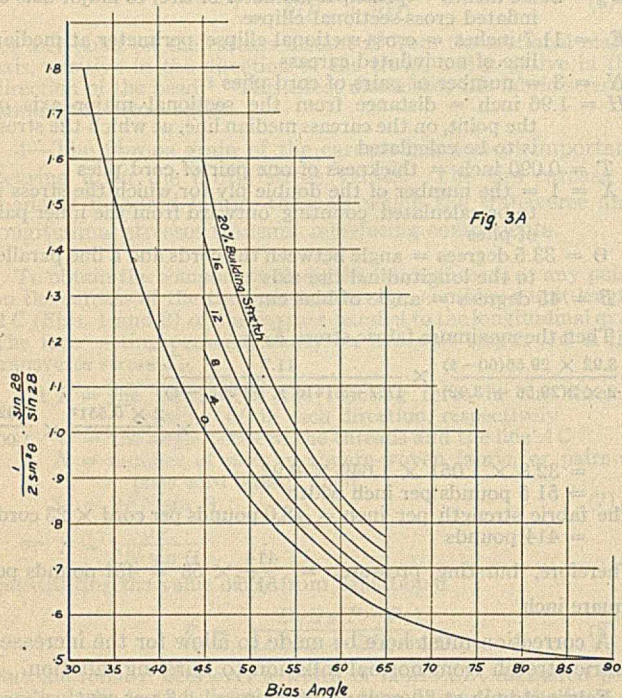


Fig. 3A

It will be interesting to calculate the pressure gradient in the tire carcass. The air presses against the inner ply with a force of 60 pounds per square inch, less the tube inflation pressure of 4 pounds per square inch. On the outside of the carcass there is no pressure. The share of the inflation pressure that each pair of plies carries, is

$$K \times \frac{2S_z}{R}$$

where  $S_z$  = fabric stress  
 $R$  = transverse radius of curvature of each pair of plies  
 $K$  = a constant

Therefore, the inflation pressure (60-4)

$$= K \left( \frac{2 \times 51.5}{\frac{3.92}{2} - 0.09} + \frac{2 \times 49.1}{\frac{3.92}{2}} + \frac{2 \times 46.7}{\frac{3.92}{2} + 0.09} \right)$$

$$= K (55.1 + 50.1 + 45.6)$$

so that  $K = 0.371$ , and the share of the inflation pressure carried by the first pair of plies

$$= 0.371 \times 55.1 = 20.5 \text{ pounds per square inch}$$

and by the second pair of plies

$$= 0.371 \times 50.1 = 18.6 \text{ pounds per square inch}$$

and by the third pair of plies

$$= 0.371 \times 45.6 = 16.9 \text{ pounds per square inch}$$

Therefore, the pressure of the first pair of plies against the second pair

$$= 60 - 20.5 = 35.5 \text{ pounds per square inch}$$

and that of the second against the third

$$= 35.5 - 18.6 = 16.9 \text{ pounds per square inch}$$

It is this pressure upon the carcass fabric that causes part of the frictional loss of power which accompanies flexure of the carcass in service.

#### STRESSES DUE TO DEFLECTION UNDER LOAD

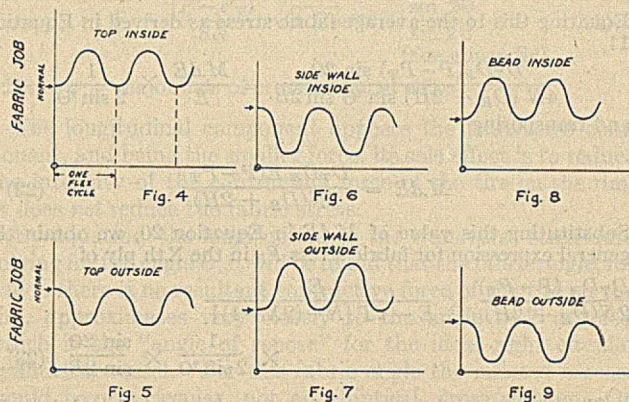
We are interested here not so much in the effect of the load upon the fabric stresses, as in the effect of the tire deflection due to the load, because the load itself does not produce any

direct stresses in the carcass plies. Its effect is to alter the distribution of the fabric stresses already set up by the inflation pressure. It has already been shown that the fabric stress is proportional to the minor axis of the tire cross section. When the tire flattens due to an applied load this minor axis decreases, and the action relieves the deflected part of the carcass of some of the inflation stress. This stress relief is not equal to the load on the tire. It is the compressed air that sustains the load, and the stress relief in the fabric of the side walls is only a secondary effect. It can be proved that the ratio of load to stress relief is  $\pi$  (see appendix).

When a tire carcass is inflated all the fabric plies are subjected to tensile stress. There are no compressive stresses in the ply planes. Cotton fabric has a high and variable tensile modulus of elasticity, but a low compressive modulus. The result is that when the inflated carcass is flexed, the neutral line shifts from the median line of the carcass toward the region of increased tensile stress. This shifting of the neutral line causes a considerably greater reduction of tensile stress in the plies on the other side of the carcass than would occur in a material whose elastic properties obeyed Hooke's law. As the flexure increases the tensile stresses in these plies drop rapidly, and in cases of overloading, and, more particularly, underinflation, the tensile stress may completely vanish and the fabric begin to buckle. The experienced tire designer knows the danger of this condition, and protects the carcass against it by molding the tire carcass with such transverse curvatures as will cause minimum flexure under operating conditions.

The foregoing statements indicate in a general way the nature of the stress disturbance due to flexure. In order that the designer may determine where the danger lies and to what extent he must protect the tire carcass against it, he must be able to determine mathematically the true extent of the disturbance.

**STRESS CYCLES**—Fig. 3 shows the cross section of a tire on a rim, with the approximate location of the neutral axis of flexure of the carcass under inflation and load, shown by the dotted line. There are three different regions of tension, and three of compression—namely, at the tread, side wall, and bead. Figs. 4 to 9 represent roughly the cycles of strain to which the carcass in these three regions is subjected as the tire rolls along the road. "Normal fabric job" means the stress due to inflation pressure alone. In the tread region of the carcass the inner ply stress is never less than the normal fabric job, but increases as the deformation due to the load stretches the fabric on the inside. Fig. 4 shows the stress



cycle to which this part of the carcass is subjected. On the outside the condition is different. The normal fabric job is the maximum tension sustained by the outer plies, so that the fabric stresses and strains decrease upon carcass deformation, as shown by Fig. 5. Figs 6 and 7 show the conditions at the side walls, and Figs. 8 and 9 at the bead. A carcass under



normal operating conditions does not fail by the action of any tensile stress so that failures in the regions indicated by Figs. 4, 7, and 8 are practically unknown. But the parts of the carcass in the compression regions on the inside of the side wall and the outside of the bead are more sensitive to abuse by the careless motorist. For a tire under normal inflation and normal loading, the amplitude of the stress cycles at these points is not great enough to extend into the compressive state. But underinflation or overloading upsets this nice balance. Underinflation alone moves all the curves downward into the trouble zone, because the normal fabric job is decreased, and the increased deflection of the carcass makes their amplitude greater. Overloading without underinflation increases the amplitude of the stress cycles, but does not

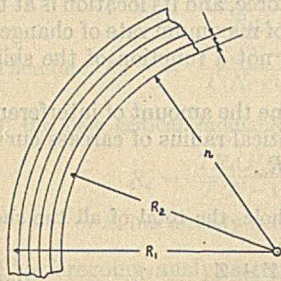


Fig. 10

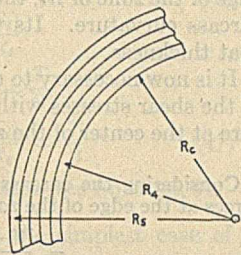


Fig. 12

affect the normal fabric job, so that, for abnormal tire deflections, the stress conditions in the fabric are probably less injurious with overloading as the cause than with underinflation.

**CRITICAL CARCASS CURVATURE**—When a tire is flexed by a load, the minimum radius of curvature of the carcass cross section usually occurs at the lower side wall, not far from the edge of the tread. It is at this point where the carcass first develops critical curvature, or curvature for which there is no stress on the inner ply. Beyond this curvature the fabric buckles. Fig. 10 represents this part of the uninflated cross section of a tire.

Let  $r$  = internal radius of the unstressed carcass  
 $R_1$  = radius to center of outer ply of unstressed carcass  
 $R_2$  = radius to center of inner ply of unstressed carcass  
 $T$  = ply thickness  
 $N$  = number of plies

$$\text{Then } R_1 = r + \frac{T}{2}(N-1/2) \quad (24)$$

$$R_2 = r + \frac{T}{2} \quad (25)$$

Let  $F_3$  = average inflation stress per ply per unit width

This stress is obtained from Equation 9 by substituting for  $D_T$  a new value of  $D_T$  decreased by the amount of the tire deflection due to the load. This load should be taken as the maximum load to which the tire may be frequently subjected. Its value may be taken in any specific instance as equal to twice normal load. This will cover the usual abnormal tire deflections due to overloading, vertical bounding, and the effect of centrifugal force on the car when turning.

Then the total carcass stress per unit width due to inflation =  $NF_3$  (26)

Now, suppose the part of the carcass under consideration to be deflected to the critical curvature, so that there is no stress on a certain sector of the inner ply, and all the stress due to inflation is sustained at that point by the outer plies. The strain values in the consecutive plies must always form an arithmetical series. The effect of shearing strains is not considered in this analysis.

Let Fig. 11 represent the elasticity curve for the fabric, and let  $AB$ ,  $AC$ ,  $AD$ , and  $AE$  represent the strains in consecutive plies, for the critical condition of no strain in the first (or inner ply) of the carcass. Then  $BF$ ,  $CG$ ,  $DH$ , and  $EK$  represent the respective

stresses in these plies. With constant inflation, the total carcass stress  $NF_3$  must always be equal to

$$BF + CG + DH + EK \quad (27)$$

Since the fabric stress does not bear any simple relation to the fabric strain, it is necessary to determine the ply stresses by this graphical method.

Let  $E_0$  = elongation  $AE$  of the outer ply  
 $R_3$  = imaginary value of radius  $R_1$  corresponding to stress  $E_0$  per ply, for the unflexed carcass

Fig. 12 represents the tire carcass flexed to critical internal radius of curvature  $R_c$ .

$$\text{Now } R_3 = R_1(1 + E_0) \quad (28)$$

$$R_4 = R_3 - T(N-1) \quad (29)$$

$$\frac{R_5}{R_4} = \frac{R_3}{R_2} \quad (30)$$

$$\text{Transposing, } R_5 = \frac{R_4 R_3}{R_2}$$

and substituting the value of  $R_3$  from Equation 28 and of  $R_2$  from Equation 25

$$R_5 = \frac{R_4 R_1 (1 + E_0)}{r + \frac{T}{2}} \quad (31)$$

Substituting this value of  $R_5$  in Equation 29

$$R_4 = \frac{R_4 R_1 (1 + E_0)}{r + \frac{T}{2}} - T(N-1) \quad (32)$$

and substituting the value of  $R_1$  from Equation 24

$$R_4 = R_4(1 + E_0) \left[ \frac{r + T(N-1)}{r + \frac{T}{2}} \right] - T(N-1) \quad (33)$$

Dividing through by  $R_4$

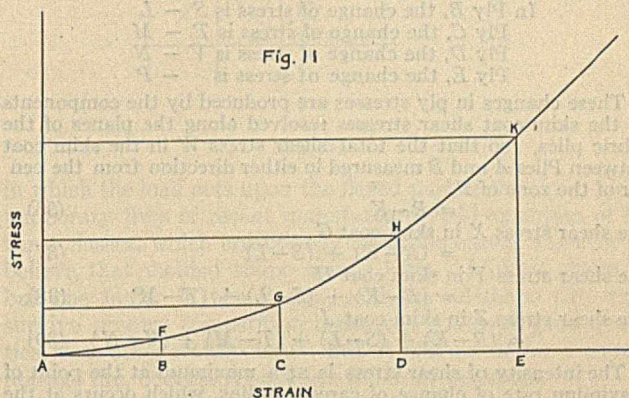
$$1 = (1 + E_0) \left[ \frac{r + T(N-1)}{r + \frac{T}{2}} \right] - \frac{T(N-1)}{R_4}$$

Therefore,  $\frac{T(N-1)}{R_4} = \frac{(1 + E_0)[r + T(N-1)] - (r + \frac{T}{2})}{r + \frac{T}{2}}$

$$R_4 = \frac{T(N-1)(r + \frac{T}{2})}{(1 + E_0)[r + T(N-1)] - (r + \frac{T}{2})} \quad (34)$$

and the critical radius  $R_c = R_4 - \frac{T}{2}$

$$R_c = \frac{T(N-1)(r + \frac{T}{2})}{(1 + E_0)[r + T(N-1)] - (r + \frac{T}{2})} - \frac{T}{2} \quad (35)$$



The less the value of  $R_c$ , the greater will be the safety for the carcass. Obviously, its value for any tire should be less than the internal radius of the carcass under the extreme deflection.

**CARCASS SHEARING STRAINS**—If the calculation of critical curvature by Equation 35 yields a value below any carcass radius to which the tire would be frequently subjected, it is not necessary to consider the modifying effect of skim-coat shears. Carcass shear diminishes the value of critical radius by allowing the fabric to move away from the zone of compression.

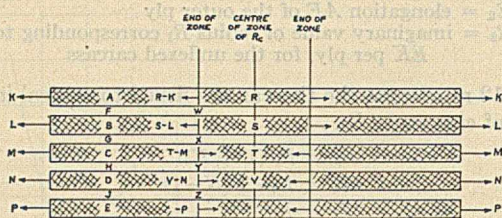


Fig. 13

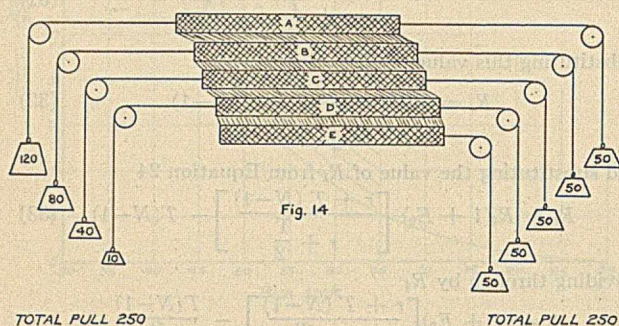


Fig. 14

Let Fig. 13 represent the developed transverse cross section of a tire in the region of critical curvature  $R_c$ . Let  $A, B, C, D,$  and  $E$  represent the carcass plies separated by the rubber skim coats  $F, G, H,$  and  $J$ , respectively. Equation 23 enables us to calculate the fabric stress in each ply of the unflexed carcass. For the purpose of this shear analysis, the term  $\frac{1}{2 \sin^2 \theta} \times \frac{\sin 2\theta}{\sin 2\beta}$  must be omitted in order to obtain the ply stress parallel to the plane of the tire cross section, and not in the direction of the threads. It is assumed that these ply stresses per unit of tire circumference at the center of the zone of  $R_c$  have been calculated and found to be  $K, L, M, N,$  and  $P$ , respectively. Now let a portion of the carcass cross section be flexed to critical radius  $R_c$ . Then the stress  $P$  on the inner ply becomes zero at the center of the zone of  $R_c$ , so that the stresses  $R, S, T,$  and  $V$  in the remaining plies must be equal in total value to  $K + L + M + N + P$  (see Equation 27). In Ply  $A$  there is a change of stress of  $R - K$ , acting away from the center of the zone of  $R_c$ .

In Ply  $B$ , the change of stress is  $S - L$   
 Ply  $C$ , the change of stress is  $T - M$   
 Ply  $D$ , the change of stress is  $V - N$   
 Ply  $E$ , the change of stress is  $-P$

These changes in ply stresses are produced by the components of the skim-coat shear stresses resolved along the planes of the fabric plies, so that the total shear stress  $W$  in the skim coat between Plies  $A$  and  $B$  measured in either direction from the center of the zone of  $R_c$ .

$$= R - K \quad (36)$$

$$\text{the shear stress } X \text{ in skim coat } G = (R - K) + (S - L) \quad (37)$$

$$\text{the shear stress } Y \text{ in skim coat } H = (R - K) + (S - L) + (T - M) \quad (38)$$

$$\text{the shear stress } Z \text{ in skim coat } J = (R - K) + (S - L) + (T - M) + (V - N) \quad (39)$$

The intensity of shear stress is at a maximum at the point of maximum rate of change of carcass radius, which occurs at the edge of the zone of  $R_c$ , and from this point its value dies away logarithmically in both directions—that is, its rate of change is equal to its actual value at any point.<sup>4</sup> This is shown by the curves in Fig. 13, or expressed mathematically:

Let  $F_0$  = maximum shear force between any two plies  
 $F_x$  = shear force at point distant  $X$  from maximum shear point  
 $e$  = base of natural logarithms  
 Then  $F_x = F_0 e^{-x}$  (40)

The rate of change<sup>4</sup> of the shear force  $F_x$   
 $= \frac{d}{dx} F_0 e^{-x} = -F_0 e^{-x}$  (41)

The total<sup>5</sup> shear force  $W$ , or  $X$ , or  $Y$ , or  $Z$   
 $= 2 \int F_x dx = 2 \int F_0 e^{-x} dx = 2 \left[ 1 - F_0 e^{-x} \right]_0^\alpha$   
 $= 2F_0$  (42)

Therefore, the maximum intensity of shear force is equal in value to one-half the total shear force, and its location is at the edge of the zone of  $R_c$ , the point of maximum rate of change of carcass curvature. Its value is not a function of the skim-coat thickness.

It is now necessary to determine the amount of interference of the shear stresses with the critical radius of carcass curvature at the center of the zone of  $R_c$ .

Considering the carcass as a whole, the total of all the shear forces at the edge of the zone of  $R_c$ .

$$= \frac{W + X + Y + Z}{2} \quad (43)$$

Individually, they die away logarithmically, so therefore collectively they do the same. Thus, their imaginary collective value  $F_x$  at the center of the zone of  $R_c$ , where  $X = \frac{\phi}{2} \left( R_c + \frac{NT}{2} \right)$ ,

$$\text{is equal to } \frac{W + X + Y + Z}{2} e^{-\frac{\phi}{2} \left( R_c + \frac{NT}{2} \right)} \quad (44)$$

where  $\phi$  = angle subtended by zone of  $R_c$

The real value of this collective shear must be zero, because there can be no transference of shear force through the center of the zone of  $R_c$  in this symmetrically flexed carcass, so that the value calculated above of shear force  $F_x$  is imaginary, and represents only the tendency of the shear forces to affect the tension distribution between the fabric plies.

Since we assumed primarily that this zone of the carcass was flexed to critical curvature, the shear force  $F_x$  can have no real effect upon the tensions in the various plies. Its tendency to increase the tension on the inner plies causes the final value of critical radius to be less than it would be had there been no shear forces present, so that the shear forces afford a protection to the fabric, but create fatiguing strains in the skim coats. The integral value of the uncompleted decay of the shear forces, which are apparently suddenly cut off at the center of the zone of  $R_c$ , does not vanish and reduce the value of the total shear forces  $W, X, Y,$  and  $Z$ . These forces remain as calculated in Equations 36 to 39, and the amount that is lost through the uncompleted decay is made up by the production of a transition spiral between the  $R_c$  zone and the unflexed part of the carcass. Undoubtedly, this spiral has a modifying effect upon the maximum value of shear.

Continuing the mathematical analysis, the imaginary value of shear force in skim coat  $Z$  at the center of the zone of  $R_c$ .

$$= \frac{ZF_x}{W + X + Y + Z} \quad (45)$$

By referring to the fabric elasticity curve in Fig. 11, we can obtain the fabric strain  $E_i$  corresponding to the imaginary stress on the inner ply as given by Equation 45.

All the data necessary to calculate the new value of critical radius  $R_c$  have now been obtained.

<sup>4</sup> Murray, "Differential and Integral Calculus," 1908, p. 65, Note 3.

<sup>5</sup> Murray, "Differential and Integral Calculus," 1908, p. 293.

Let  $R_6$  = carcass radius to center of inner ply  
 $R_7$  = carcass radius to center of outer ply

$$\text{Then } \frac{R_7}{R_6} = \frac{R_5}{R_4(1-E_i)} \quad (46)$$

$$\text{But } R_7 = R_5 + T(N-1)$$

$$R_6 = R_4 + T(N-1)$$

$$\text{Therefore, } \frac{R_6 + T(N-1)}{R_6} = \frac{R_4 + T(N-1)}{R_4(1-E_i)}$$

simplifying

$$1 + \frac{T(N-1)}{R_6} = \frac{1}{1-E_i} + \frac{T(N-1)}{R_4(1-E_i)}$$

$$\frac{T(N-1)}{R_6} = \frac{T(N-1)}{R_4(1-E_i)} + \frac{E_i}{1-E_i}$$

$$= \frac{T(N-1) + E_i R_4}{R_4(1-E_i)}$$

$$\text{Therefore, } R_6 = \frac{TR_4(N-1)(1-E_i)}{T(N-1) + E_i R_4}$$

and the new critical radius  $R_c = R_6 - \frac{T}{2}$ .

$$R_c = \frac{TR_4(N-1)(1-E_i)}{T(N-1) + E_i R_4} - \frac{T}{2} \quad (47)$$

The value of  $R_4$  has already been calculated (see Equation 34).

The foregoing analysis represents the simplest case of a flexed carcass, in which the carcass curvature on either side of the zone of critical curvature is equal to the original molded curvature. In this case there is no interference of other zones of curvature change.

Fig. 14 presents a diagrammatic picture of the ply stress conditions in the critically flexed carcass. The weights on the right side represent the uniform ply tensions outside of the zone of flexure, and those on the left the unbalanced ply stress conditions due to flexure. The sum total of all the weights in each case is the same, and represents the inflation stress acting on the carcass.

In order that we may get a better conception of the relative values of critical curvatures as calculated by Equations 35 and 47, let us consider the special case of a 5-ply square-woven fabric tire, of ply thickness 0.040 inch and internal carcass radius 1.5 inches. Assuming that the fabric stretch  $E_o$  is 8 per cent, we would find the critical carcass curvature, as calculated by Equation 35, which neglects the action of skim-coat shears, to be 0.88 inch. Calculating the critical curvature by Equation 47, which takes skim-coat shear into consideration, and assuming the zone of  $R_c$  to be 2 inches wide, we would find a critical curvature of 0.79 inch. The difference between the two values indicates the extent to which shear reduces the fabric fatigue.

The effect upon the fabric stresses in a whole tire carcass under the combined action of flexure and shear is, however, more complex than the simple case analyzed above, but an accurate determination can be made by elaborating upon the fundamental analysis. It becomes necessary to make a "shear survey" of the whole tire carcass. If the designer's objective is the design of a completely new tire, it is necessary for him to get his conception of the whole problem by making shear surveys upon some tires already manufactured. This can be done by taking measurements upon the tire under all the required conditions—viz., molded, inflated, and loaded—and under any abnormal conditions that the designer may deem necessary. The measurements may be made by dimension scaling, or by taking plaster casts of the outside of the tire, or of the inside. The writer cannot go into the details of this work here, but when once the principles of the work are clearly fixed the methods may easily be planned. The designer must remember, however, that the carcass curvatures are functions of many variables, chief of which are fabric angle, ratio of extreme to cross-sectional tire diameter, tread radius, and

cross-sectional disposition of tread-stock. For the latter two reasons tread design is closely related to carcass stress analysis.

Fig. 15 represents a typical curvature analysis for a tire carcass. The abscissas represent displacement along the neutral axis of the carcass from the point opposite the center of the tread to the rim contact point. The ordinates represent the curvature changes under the given conditions of inflation and load.

Let  $r_o$  = original carcass radius of curvature

$r_x$  = deflected radius at any point  $X$

$$\text{Then the change of curvature} = \frac{1}{r_x} - \frac{1}{r_o} \quad (48)$$

The curvature changes in the tread and bead regions are negative, and at the side walls positive.

The maximum change of curvature occurs in the region  $AB$ . Its value is  $AF$ . Were it not for the disturbing effect of the unsymmetrical shears at either end of this region, the maximum shift of the neutral axis of the carcass would occur at the point  $C$ , midway between the points  $A$  and  $B$ . But owing to these unsymmetrical shears, the point is shifted to  $G$ , at which point the two shears neutralize each other, as shown by the intersection of curves  $HK$  and  $LM$ , representing the logarithmic decrement loci of the shears  $AD$  and  $BE$ . The distribution of the total carcass stress among the plies may now be determined by a method similar to that by which the critical curvature was previously calculated, allowance being made for the effect of shear.

In order that the reader may get some idea of the extent to which the designed cross-sectional shape of a tire may affect the carcass tension and shear stresses under inflation and load, Figs. 16, 17, and 18 have been drawn to represent diagrammatically the stress conditions corresponding to different molded shapes. The weight marked "Inflation" suspended over the pulley represents the way in which the inflation stress acts on the carcass, and the weight marked "Load," the way

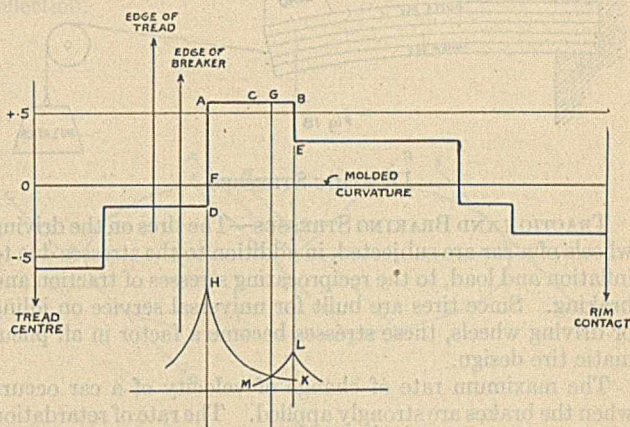


Fig. 15

in which the load acts upon the flexed part of the tire. Contemporary tires of recent manufacture yield examples of all three classes, which erroneously leads the casual observer to believe that molded shape means little. Molded shape is but one factor in tire design, and the off-shape tire may survive present competition because it possesses good qualities from other standpoints. But it will never be a super-mileage tire, because it possesses inherent weakness.

**SKIM-COAT SHEAR STRAINS**—This subject is so closely connected with fabric stress analysis that the method of calculating the value of maximum shear strain will be given. It has been calculated that the maximum intensity of shear force  $F_s$  is equal to one-half of the total shear force (Equation 42).

Let  $M_s$  = skim-coat modulus of elasticity up to the usual skim-coat strain

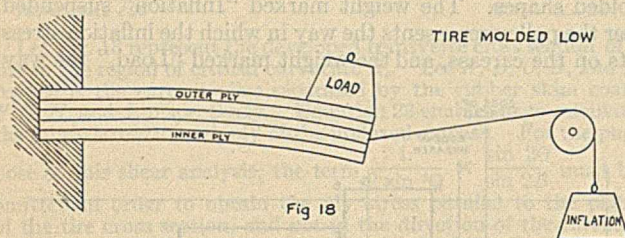
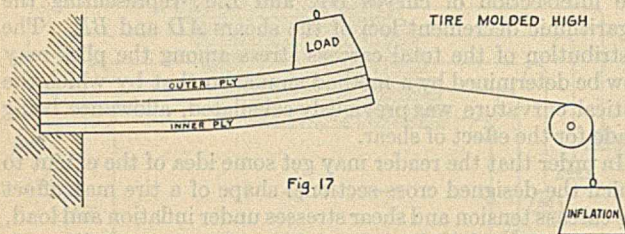
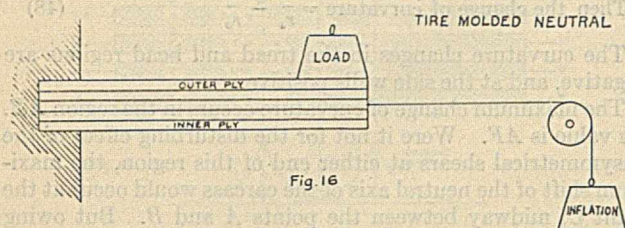
$\omega$  = angular shear of skim coat

$$\text{Then } F_s = M_s (\sec \omega - 1) \sin \omega \quad (49)$$

$$= M_s (\tan \omega - \sin \omega) \quad (50)$$

From Equation 50 the shear angle can be calculated, and the skim-coat elongation =  $\sec \omega - 1$  (51)

In the absence of definite data on fatigue of the bond between the skim-coat rubber and the fabric, the designer must base his critical values upon the calculated skim-coat elongations in tires which have established a known performance.



#### DYNAMIC STRESSES

**TRACTION AND BRAKING STRESSES**—The tires on the driving wheels of a car are subjected, in addition to the stresses due to inflation and load, to the reciprocating stresses of traction and braking. Since tires are built for universal service on idling or driving wheels, these stresses become a factor in all pneumatic tire design.

The maximum rate of change of velocity of a car occurs when the brakes are strongly applied. The rate of retardation may be carried to the skidding point of the tire on the road surface. At this point the retarding force acting on the tire is equal to the product of the weight sustained by the tire and the coefficient of friction between the tire and the road surface. This coefficient may have a maximum value as large as unity. The actual weight supported by the rear tires when braking the car is decreased by the tendency of the car to overturn forward, similar to the tendency to overturn sideways when turning a corner. Therefore, the virtual coefficient of friction based on the weight sustained by the tire at rest or in uniform motion will be less than its actual value based on the real weight supported when braking. The reverse effect takes place when the speed of the car is accelerated. The inertia of the car causes a tendency to overturn backward, and extra weight is thrown on the rear wheels, so that cars with short wheel-bases assume that peculiar crouching attitude when started suddenly.

The value of the virtual coefficient of friction in this case is greater than its actual value.

Let  $W$  = standard recommended loading for the tire

$\mu$  = virtual coefficient of friction between tire and road surface

Then the maximum accelerating or braking force  $F_M$  on the tire =  $W\mu$  (52)

If the rate of acceleration or deceleration is known and it is required to find the corresponding force  $F_N$  acting on the tires

let  $a$  = rate of acceleration or deceleration

$W_c$  = car weight

$g$  = acceleration due to gravity

$$\text{Then } F_N = \frac{W_c a}{2g} \quad (53)$$

If the car speed and the power transmitted by the engine to the tires are known, the tractive force  $F_T$  per tire can be calculated.

Let  $V$  = car velocity in miles per hour

$$\text{Then the tractive force } F_T \text{ per tire} = \frac{187.5 \text{ h. p.}}{V} \quad (54)$$

If a car ascends a grade of  $G$  per cent at uniform speed, the tractive force  $F_G$  per tire =  $\frac{W_c G}{200}$  (55)

and must be added to the tractive force  $F_T$  to obtain the total force upon the tire.

From these equations we can determine the values of this class of dynamic stresses under various conditions of performance on the road. It is necessary to assure sufficient protection to the carcass to withstand, not only the greatest of these stresses, but also the fatiguing action of all of them. Having determined their numerical values, it is then necessary to know the shape and size of the area of contact between the tire and the road surface.

Let the ellipse in Fig. 19 represent the contact area between the tire and the road. It is approximately elliptical in shape, the major axis being parallel to the direction of motion of the tire. Neglecting shear displacement in the rubber, the traction or braking force is transmitted uniformly to every unit area of fabric lying directly over the road contact area. Let  $OA$  and  $OB$  represent the two directions of the fabric threads in the carcass. By drawing  $CD$  and  $EF$  parallel to  $OA$  and tangent to the road contact ellipse, we obtain the zone of fabric threads lying parallel to  $OA$  that are affected by the stresses under consideration. By drawing two similar lines parallel to  $OB$ , we obtain the other zone of fabric threads similarly affected. The line  $GH$  represents the length of extended major axis intercepted by these parallel lines. To obtain the maximum force per unit width of fabric, it is necessary to take two points on the major axis unit distance apart, and equidistant from the point  $O$ , and draw two lines,  $KL$  and  $MN$ , through these points and parallel to  $OA$ .

The stress intensity per unit area of road contact ellipse

$$= \frac{F_M}{A_E} \quad (56)$$

where  $A_E$  = area of road contact ellipse

Therefore, the stress acting on the area  $A_M$  between the lines

$$KL \text{ and } MN = \frac{A_M F_M}{A_E} \quad (57)$$

Resolving this stress along the direction of the fabric threads, we get the stress intensity per unit width of carcass

$$= \frac{A_M F_M}{2A_E \sin \theta \cos \theta} \quad (58)$$

Dividing the stress equally among the carcass plies, and correcting for fabric distortion, we get the stress  $F_D$  per unit of original width of fabric

$$= \frac{A_M F_M}{2N A_E \sin \theta \cos \theta} \times \frac{\sin 2\theta}{\sin 2B} \quad (59)$$

But  $\sin 2\theta = 2 \sin \theta \cos \theta$

$$\text{Therefore, } F_D = \frac{A_M F_M}{N A_E \sin 2B} \quad (60)$$

For  $F_M$  we may substitute  $F_N$ ,  $F_T$  or  $F_G$  according to the conditions under which we wish to calculate the dynamic stress in the fabric. This equation shows that the fabric stress is in-

dependent of the stretch applied to the fabric in building the carcass.

Let us, for example, calculate the maximum fabric stress at the edge of the road contact ellipse in a 33 x 4 S. S. cord tire, when the brakes are strongly applied.

Let  $W = 850$  pounds

$\mu = 1.0$

Then  $F_M = 850 \times 1.0 = 850$  pounds (Equation 52)

Let the stress on area  $A_M = 150$  pounds (Equation 57)

$N = 3$ , and  $B = 45^\circ$

Then the fabric stress =  $\frac{150}{3 \times \sin 90^\circ}$  (Equation 60)  
= 50 pounds per inch width

Every part of the tire carcass, as it revolves on the wheel and makes contact with the road surface, is subjected to the simultaneous action of the dynamic stress of traction or braking and the stress due to flexure under load. The latter stress may be determined by the method of calculation outlined under "Stresses Due to Deflection under Load." This stress is at a maximum in the outer ply of the carcass, and has a value  $EK$  (Equation 27), so that the maximum fabric stress due to these two simultaneous stresses is equal to the sum of the two stresses.

#### CENTRIFUGAL STRESSES

Centrifugal stress is generated in a tire owing to the action of its mass, which tends to pull away from the center about which the tire revolves. It is a function of the mass of the tire, of the extreme diameter, and of the speed at which the tire revolves. Its value is a minimum in that part of the carcass directly under the center of the tread, and is cumulative toward the bead region. Therefore, in a straight-side tire the bead wires must finally supply the total reaction to this force.

The centrifugal force acts in a direction parallel to the minor axis of the cross-sectional ellipse, and hence increases this minor axis. Its action has the characteristic of a directional inflation pressure away from the center of rotation of the tire, and thus it decreases the deflection of a tire when the latter revolves on the road.

The total mass of a tire is made up of (1) casing, (2) inner tube, (3) compressed air, and (4) flap (if used). In calculating the centrifugal stress which the bead must resist, all these parts must be taken into consideration; in other cases only part is taken, depending upon the location of the point at which the stress is to be determined.

The elementary equation of centrifugal force is

$$F_c = \frac{Wv^2}{gR} \quad (61)$$

where  $F_c$  = centrifugal force

$W$  = weight of the body

$v$  = linear velocity

$g$  = acceleration due to gravity

$R$  = radius of rotation to center of gravity of body

Adapting this equation to the conditions in a tire, let Fig. 3 represent the tire cross section and  $X-X$  the point at which we wish to determine the centrifugal ply stress.

Let  $W_s$  = weight of tire above lines  $X-X$

$W_T$  = weight of tube lying between lines parallel to the minor axis of cross-sectional ellipse, and passing through the points  $O$ , the intersection points of the lines  $X-X$  and the neutral axis of the carcass

$W_A$  = weight of air between these lines

$W_F$  = weight of flap between these lines

Then the total mass  $M_T$ , which generates the centrifugal force imposed upon the tire at the zone  $X-X$ , is

$$M_T = \frac{W_s + W_T + W_A + W_F}{g} \quad (62)$$

Let  $R_G$  = radius of gyration of this total mass

Then the moment of inertia  $I$  of the mass  $M_T$  is

$$I = M_T R_G^2 \quad (63)$$

and the centrifugal force becomes

$$F_c = \frac{I}{RG} (2\pi r. p. s.)^2 \quad (64)$$

where r. p. s. = speed of tire in revolutions per second

If the tire speed is calculated from the speed of the car on the road, allowance must be made for the decreased tire diameter at the road contact surface, and if the tire on the driving wheel is under consideration a correction must be made for the relative slip between the tire and the road surface due to the effect of traction.

The total centrifugal force  $F_c$  having been determined, its intensity per unit width of carcass ply must be found. Referring to Fig. 3, it will be seen that the force  $F_c$  is distributed over two circumferential zones  $X-X$ , one on each side of the tire.

Let  $R_z$  = radius of revolution of point  $O$

Then the total width of carcass fabric over which the force  $F_c$  is distributed is

$$4\pi NR_z \quad (65)$$

If  $A$  = angle between minor axis of cross-sectional ellipse and the tangent to ellipse at intersection point  $O$  of line  $X-X$

then the centrifugal stress intensity per unit width of carcass ply becomes

$$\frac{F_c}{4\pi NR_z \cos A} \quad (66)$$

Expressing this stress intensity in terms of stress per unit of original fabric width, the fabric stress  $S_c$  becomes

$$S_c = \frac{F_c}{4\pi NR_z \cos A} \times \frac{1}{2 \sin 2\theta} \times \frac{\sin 2\theta}{\sin 2B} \quad (67)$$

The effect of this stress need not be considered in connection with inflation and deflection stresses, because its action is considerably reduced at that part of the tire in contact with the road. It is of importance principally in the calculation of bead wire stress, and for its effect upon the dynamic tire deflection.

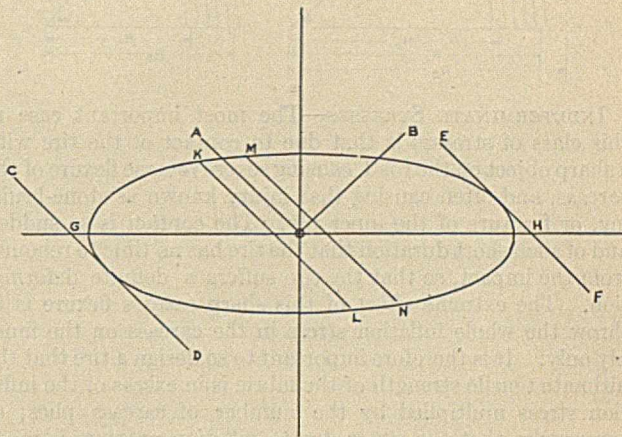


Fig. 19

The centrifugal force may be expressed in terms of equivalent inflation pressure as follows:

Calculating the centrifugal force  $F_c$  for the mass of the tire, tube, flap, and air, but excluding the bead wires, and distributing this force over the plane generated by the rotation of the major axis of the cross-sectional ellipse about the axis of rotation of the tire, we get the equivalent inflation pressure  $P$ .

$$P_c = \frac{F_c}{\pi D R^2} \quad (68)$$

This virtual inflation pressure will decrease the tire deflection relative to the road surface by the same amount as an actual pressure increase above the normal inflation pres-

sure.<sup>6</sup> It does not necessarily decrease the fatigue in the carcass. The centrifugal force elongates the minor axis of the cross-sectional ellipse in the part of the carcass not in contact with the road by approximately the same amount as it increases this axis in the road contact region, so that the total variation in length of the minor axis per cycle is not appreciably changed.

and if  $m$  equals the ratio of stress to strain per unit cross-sectional area of tube stock corresponding to the strain of complete inflation of the tube, then the force per unit of tube length resisting the inflation pressure equals the elastic modulus of the stock times the cross-sectional area of tube times the strain per unit of transverse perimeter. Represented symbolically, this force equals

$$mt \frac{L_c - L_T}{L_T} \tag{69}$$

Let  $P_T$  = air pressure required to inflate the tube to fill the interior of the carcass

Then, according to Equation 1, the transverse stress per inch of tube length

$$= \frac{P_T \times \text{tube cross-sectional inflated diameter}}{2} = \frac{P_T L_c}{2\pi} \tag{70}$$

and equating the expressions 69 and 70, which represent the same force in different terms,

$$\frac{P_T L_c}{2\pi} = mt \frac{L_c - L_T}{L_T}$$

and transposed

$$P_T = 2\pi mt \frac{L_c - L_T}{L_c L_T}$$

PROOF OF EQUATION 12—Fig. 20 represents the fabric parallelograms referred to in connection with Equation 10. The sides of these parallelograms are all equal, because the distortion alters only the internal angles.

Let  $S$  = ratio of stretched to unstretched length of the fabric ply at the extreme ply diameter.

Then it may readily be seen by referring to Fig. 20 that the relation of the fabric angle  $\theta$  to the bias angle  $B$  is

$$\cos \theta = S \cos B \tag{71}$$

This relation holds true only at the extreme ply circumference. To establish this relation at any other point on the carcass, the fabric distortion at that point must be considered. The stretch of the fabric ply at any point (such as at  $A$  in Fig. 21) to conform to the shape of the core upon which the tire is built is proportional to the distance of the point from the center of rotation of the core, so that if  $S$  is the circumferential fabric distortion at the extreme ply diameter, then the circumferential distortion at the point  $A$  is

$$S \frac{D_R + 2H}{D_R + D_T} \tag{72}$$

Equation 71 thus generalized becomes

$$\cos \theta = S \cos B \left( \frac{D_R + 2H}{D_R + D_T} \right)$$

PROOF OF EQUATION 13—The ellipse in Fig. 22 represents the cross-sectional median line of a tire carcass.

Let  $a$  = major axis of ellipse

$D_T$  = minor axis of ellipse

Then the area of the cross-sectional ellipse

$$= \frac{\pi}{4} a D_T \tag{73}$$

and the force tending to elongate the carcass

$$= (P - P_T) \frac{\pi}{4} a D_T \tag{74}$$

This force acts over whole perimeter of the carcass cross section. The length of the perimeter of the cross-sectional ellipse

$$= \pi \sqrt{a D_T} \tag{75}$$

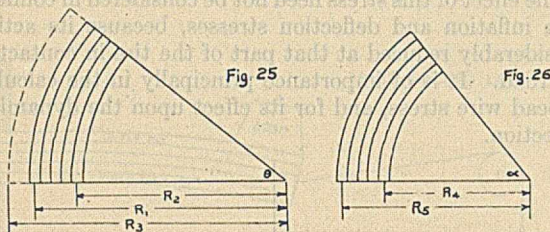
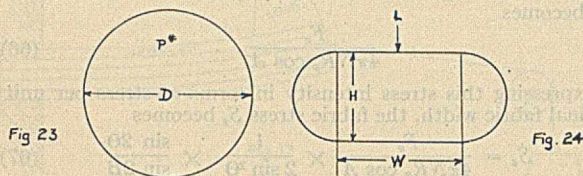
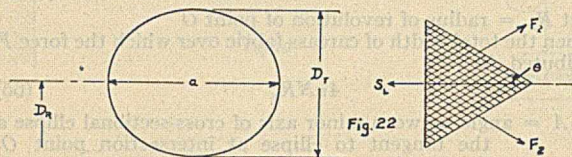
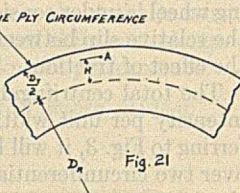
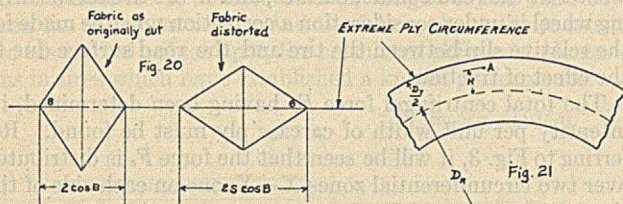
Therefore, the longitudinal stress  $S_L$  per unit of perimeter

$$\begin{aligned} &= \frac{(P - P_T) \frac{\pi}{4} a D_T}{\pi \sqrt{a D_T}} \\ &= \frac{(P - P_T) \sqrt{a D_T}}{4} \end{aligned} \tag{76}$$

This stress is distributed among all the plies of the carcass, so that the stress per ply in one direction

$$= \frac{(P - P_T) \sqrt{a D_T}}{8N} \tag{77}$$

Resolving this stress along the direction of the threads, we



INDETERMINATE STRESSES—The most important case in this class of stresses is that due to contact of the tire with a sharp object on the road, causing severe reverse flexure of the carcass, and often causing that injury known as stone-bruising, or fracture of the inner ply. The contact is so sudden and of such short duration that the tire has no time to rebound from the impact, so that the tire suffers a definite deformation. The extreme effect of this sharp carcass flexure is to throw the whole inflation stress in the carcass on the inner ply only. It is therefore important to so design a tire that the ultimate tensile strength of the fabric is in excess of the inflation stress multiplied by the number of carcass plies; or conversely, that the stress due to inflation pressure is made less than the ultimate tensile strength of the fabric divided by the number of plies. The rigidity of the carcass adds somewhat to the stress on the inner ply during flexure, so that the safety factor should not be shaded too closely to the critical value.

APPENDIX

PROOF OF EQUATION 4 IN DETAIL—When the tube is inflated to fill the interior of the tire carcass, the outer surface of the tube coincides with the inner surface of the carcass. Therefore, the external cross-sectional perimeter  $L_T$  of the tube is stretched until it equals the internal cross-sectional perimeter  $L_c$  of the carcass, so that the strain per unit of transverse perimeter of tube equals

$$\frac{L_c - L_T}{L_T}$$

<sup>6</sup> J. Soc. Automotive Eng., 11, 438 (1922)

obtain the stress per unit width of fabric measured perpendicularly to the threads of

$$\frac{(P-P_T)}{8N} \sqrt{aD_T} \sec^2 \theta \quad (78)$$

and correcting for the thread concentration due to fabric distortion, we get the real fabric stress

$$F_2 = \frac{(P-P_T)}{8N} \sqrt{aD_T} \sec^2 \theta \frac{\sin 2\theta}{\sin 2B}$$

**PROOF OF LOAD RELATION TO FABRIC STRESS RELIEF**—Fig. 23 represents diagrammatically the cross section of an inflated carcass, having a diameter  $D$  and an inflation pressure  $P$ .

According to Equation 1, the transverse fabric stress =  $\frac{PD}{2}$ .

Fig. 24 represents the same carcass deflected under the load  $L$  per unit of carcass length.

$$\text{The new fabric stress} = \frac{PH}{2} \quad (79)$$

$$\text{So that the stress relief due to flexure} = \frac{PD}{2} - \frac{PH}{2} \quad (80)$$

$$= \frac{P}{2}(D-H) \quad (81)$$

Now, because the carcass retains the same transverse perimeter

$$2W = \pi D - \pi H \quad (82)$$

$$\text{or } W = \frac{\pi}{2}(D-H)$$

$$\text{But } W = \frac{L}{P} \quad (83)$$

$$\text{So that } L = \frac{\pi P}{2}(D-H)$$

Therefore, the ratio of load to stress relief

$$\begin{aligned} & \frac{\pi P}{2}(D-H) \\ &= \frac{P}{2}(D-H) \\ &= \pi \end{aligned} \quad (84)$$

**PROOF OF EQUATION 30 THAT  $\frac{R_5}{R_4} = \frac{R_3}{R_2}$** —Fig. 25 represents a sector of unstressed carcass subtended by the angle  $\theta$ .

$R_1$  = radius to center of outer ply

$R_2$  = radius to center of inner ply

$R_3$  = imaginary value of radius  $R_1$ , if the tire were simply inflated until the stress per ply were equal to that sustained by the outer ply under critical curvature conditions. (This has already been explained in the text. See Equation 27.)

Now let Fig. 26 represent the same sector of carcass flexed to critical curvature. The subtended angle  $\alpha$  is greater than the angle  $\theta$ .

Since the stress on the outer ply is the same in both Figs. 25 and 26, then the outer ply lengths are the same, so that

$$R_3\theta = R_5\alpha \quad (85)$$

Similarly, the inner ply lengths are the same, so that

$$R_2\theta = R_4\alpha \quad (86)$$

Therefore, combining Equations 85 and 86

$$\frac{R_5\alpha}{R_4\alpha} = \frac{R_3\theta}{R_2\theta} \quad (87)$$

and simplifying

$$\frac{R_5}{R_4} = \frac{R_3}{R_2} \quad (88)$$

## The World's Dairy Congress

**A**N International Congress on dairying, held in this country October 2 to 10, was attended by 1800 delegates, including over 200 from 43 foreign countries.

At the opening sessions in Washington, October 2 and 3, the delegates were welcomed by Secretary Hughes and addresses were made by Secretaries Wallace and Hoover. Additional sessions were devoted to papers on international trade and the development of the dairy industry. On October 4 the Congress adjourned to Philadelphia, where a demonstration was given of the methods used by the National Dairy Council in educating the public to the nutritive value of milk. From Philadelphia special trains took the delegates to Syracuse, where the National Dairy Exposition was held. October 5, 6, 8, 9, and 10 were given over to technical papers on topics related to the dairy industry.

About 245 papers were presented at the 27 sessions into which the Congress was divided. Abstracts of the papers in English, French, German, and Spanish were available at registration, and full papers and proceedings will be published by the Government. Three of the sessions were devoted to the nutritional side of the milk question, and included papers by McCollum, Mendel, Blackham, Sherman, Block, and Pirquet. R. M. Allen and Chas. A. Glabau discussed the question of the use of milk and milk powders in the baking industry, both from the standpoint of the increase in nutritive value and the effect of the addition of milk solids on the size and quality of the loaf. In the section on equipment two papers discussed the use of various metals in the handling of milk and the manufacture of milk products.

In the session devoted to the transportation of milk considerable attention was given to the use of steel tanks for both automobile and railroad shipments. A collection of papers on milk secretion and the nutrition of dairy cows included contributions by Porcher, Isaachsen, Koestler, Forbes, and Meigs. H. M.

Evans discussed the occurrence and distribution of a new dietary factor essential to reproduction.

Additional papers of interest to chemists appeared in various sessions of the Congress. These included a paper by L. L. Van Slyke on "The Chemistry of Casein," by L. S. Palmer on the "Chemistry of Milk and Milk Products from a Colloidal Standpoint," by Alan Leighton and P. N. Peter on "Factors Influencing the Crystallization of Lactose," by A. Miyawaki on "The Keeping Quality of Sweetened Condensed Milk," by H. H. Somer on "The Heat of Coagulation of Milk," by A. Leighton and E. F. Deysher on "Factors Influencing the Heat Coagulation of Milk and the Thickening of Condensed Milk," by G. C. Supplee on "The Keeping Quality of Dry Milk," by G. E. Holm and G. R. Greenbank on "The Keeping Quality of Butterfat with Special Reference to Milk Powder," and by H. Jephcott and N. Ratcliffe on "Fat in Commercial Casein." The splendid program was largely due to the work of L. A. Rogers, of the Dairy Division, U. S. Department of Agriculture.

Syracuse University at a special convocation conferred the degree of doctor of science on C. J. Hastings, of Canada; C. Orla-Jensen, of Denmark; Masayoshi Sato, of Japan; Haakon Isaachsen, of Norway; Gerald Leighton, of Scotland; Robert Burri, of Switzerland; Robert Stenhouse Williams, of England; Charles Borchers, of France; and Sir Arnold Theiler, of South Africa. The degree of doctor of laws was conferred on Cesares Longobardi, of Italy, and H. E. Van Norman, president of the Congress.

A number of excursions were arranged for the delegates, both before and following the Congress, to farms, dairy manufacturing establishments, and educational institutions. These included an automobile trip ending at Ithaca for the dedication of the new dairy building of Cornell University and a long trip to the Pacific Coast.

# The Absorption of War Gases by Rubber and Rubberized Fabric<sup>1</sup>

By Thomas M. Rector

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## CHLOROPICRIN IN AIR

**C**LEAN-CUT practical methods were available for all the common war gases when present in amounts exceeding 25 parts per million of air. Below this concentration no chemical method could be depended upon. Chloropicrin, when present in amounts exceeding 2 parts per million in air causes involuntary closing of the average eye. It was noted, however, that a measurable interval of time elapsed between exposure to the gas and the closing of the eye. Further tests showed that this time interval varied sharply with the concentration of the gas, and that this variation could be used to determine chloropicrin concentration between 1 part per million and 30 parts per million with enough accuracy for the purpose of the investigation.

Using these facts as a basis, the following method was evolved:

**APPARATUS**—Before determinations of chloropicrin concentrations can be made physiologically, the eyes of the operators must be calibrated by exposure to known concentrations of gas in air and recording the time of the eye reaction. For this work the following apparatus is required:

1—A device for producing a chloropicrin-air mixture of constant concentration consisting of a source of compressed air, a sulfuric acid drying bottle, an empty bottle as a trap, and a "bubbler" bottle of chloropicrin in a bath of melting ice. (Fig. 1)

2—A glycerol-lubricated, ground-glass syringe for transferring gas.

3—A round glass bulb with a short neck which fits into the eye like an eye cup. This should be fitted with a heavily paraffined rubber stopper containing a short piece of capillary tubing. The bore of the capillary should be a trifle larger than the syringe needle.

4—A stop watch for recording time of eye reaction.

**METHOD**—The apparatus having been assembled, a sample ranging from 0.1 to 2 cc. is withdrawn from the bubbler with the syringe and introduced into the bulb through the capillary. The bulb is then shaken a few times to mix the gas, the stopper is quickly removed, and the neck of the bulb is placed over the closed eye of the subject. He then opens his eye normally, at the same time starting the stop watch. Within from 3 to 30 seconds, depending, of course, upon the concentration of gas, the subject will have an overpowering impulse to close his eye. At this point the stop watch is stopped and the time recorded. A series of tests should be run, varying the concentration up to the limit of endurance of the subject. Convenient concentrations to test are 2.5, 5, 7.5, 10, 15, 20, and 25 parts per million. From the data thus obtained a calibration curve can be drawn plotting the concentration in parts per million against the time of the

*Soon after the adoption of the Akron Tissot and Kops Tissot face pieces for the American gas mask, Major R. G. Pierce, of the Physiological Division of the Chemical Warfare Service, made the discovery that practically every face piece of these types, no matter how well fitted, leaked air in measurable amounts. The amount of "leak-in" varied from a few cubic centimeters of air per minute to several hundred per minute. This discovery caused a great deal of controversy in the chemical warfare laboratories. Those who doubted that the face pieces leaked, immediately raised the question: "Why aren't the men gassed if the face pieces leak?"*

*The investigations reported in this paper were made for the purpose of answering this question. The results of the experiments are reported at this time more on account of the unique methods employed and their possible utilization in other fields, than for their bearing on gas-mask development.*

eye reaction in seconds. (Fig. 2) The physiologists may be interested in knowing that the eyes of different subjects varied greatly but both eyes of the same subject reacted similarly as far as could be determined.

Having calibrated the eye of the subject, one can determine the concentration of chloropicrin in any vessel or room by simply recording the time to the eye reaction and reading the concentration by reference to the calibration curve of his eye.

## ABSORPTION OF CHLOROPICRIN BY FACE PIECES

In preliminary experiments made at the Lakeside Hospital the observation was made that amounts of chloropicrin and phosgene up to 50 parts per million disappeared within 5 minutes when injected into the face piece of both Akron Tissot and Kops Tissot masks. These tests were made with the subject breathing freely into the outer air through a tube, so that the air within the face piece was not changed. The physiological method described made it possible to follow the rate of disappearance of the chloropicrin with considerable accuracy.

For the purposes of the work Akron Tissot and Kops Tissot masks were fitted with the old-fashioned mouthpiece and nose-clip, so that the air inside the face piece would not be changed during the experiment. In some of the tests wherein the interior of the masks was coated with gas-resistant substances, it was found best to attach the mask to an empty bottle. The dead space in the masks was measured

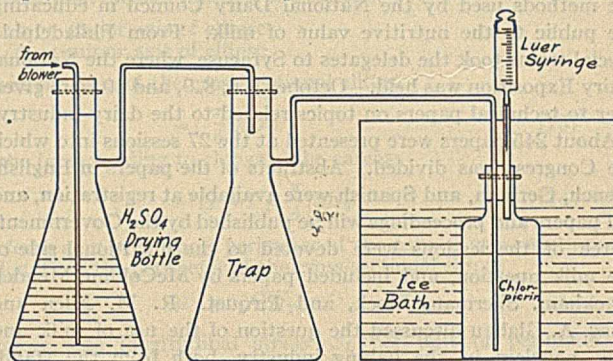


FIG. 1—APPARATUS FOR OBTAINING CONSTANT CONCENTRATIONS OF CHLOROPICRIN

by displacement with water while attached to the subjects or to the empty bottle. The gas was put into the face piece by means of a syringe, as described above. After the gas had been put into the mask, the subject was required to shake his head in order to mix gas and air. When the bottle method was used, the entire apparatus was shaken.

When the masks were attached to subjects, the subjects themselves made the determinations at intervals. It was

<sup>1</sup> Received October 19, 1922.



found that a man wearing a mask could make four determinations without removing it. If more than this were attempted, the eyes watered to such an extent that the results were not accurate. When the method of attaching the mask to a bottle was used, the determination was made by applying the eye to the inhalation tube of the mask.

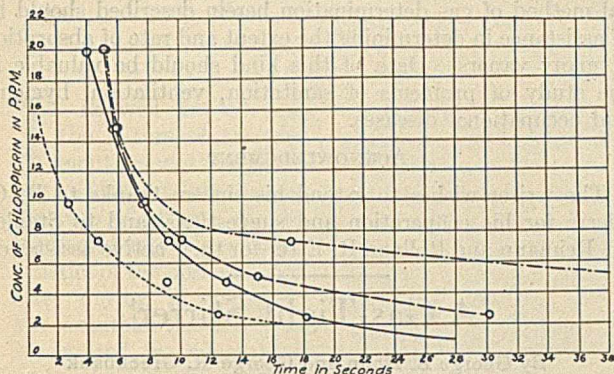


FIG. 2—CALIBRATION CURVES OF EYES FOR CHLOROPICRIN

Tests by the foregoing methods were made on both Akron and Kops masks, both dry and with their interior surfaces wet with water. (Fig. 3) A special test was also made on an Akron mask coated with a 5 per cent gelatin solution, applied uniformly on the interior surface of the mask and allowed to cool to a jelly. The tests were made before the gelatin dried to a film. The result of this test is shown in Table I.

TABLE I—ABSORPTION OF CHLOROPICRIN BY GELATIN-COATED AKRON TISSOT FACE PIECE

Time Minutes	Gas Unabsorbed P. p. m.
At start	30
2	23.5
4	17.0
7	7.5
10	6.5
15	5

#### ABSORPTION OF CHLOROPICRIN BY FACE-PIECE MATERIAL

The experiments described showed that gas introduced into the face pieces of gas masks disappeared very rapidly. The fact that wetting the face piece with water and gelatin solution retarded this absorption indicated very strongly that the face-piece material was playing a strong part in absorbing the gas. In order to determine definitely the extent of this absorption, the following experiments were made:

**MATERIALS AND APPARATUS**—The face-piece material tested was cut from an Akron Tissot mask. The outer cloth

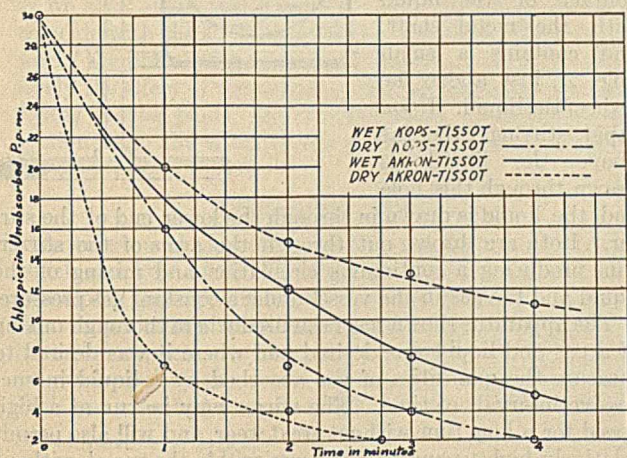


FIG. 3—CHLOROPICRIN ABSORPTION CURVES OF MOIST AND DRY KOPS TISSOT AND AKRON TISSOT MASKS, WITH FACE PIECES ALONE FITTED TO SUBJECT

covering of the rubber was stripped off. For each absorption test fresh pieces were cut, measured, and their area calculated.

The absorption tests were made in a lamp bulb with its neck shaped like an eye cup, as described above. The bulb was fitted with a heavily paraffined rubber stopper provided with a capillary glass tube through which known quantities of gas were introduced by means of an all-glass syringe. Control tests were made which showed that the paraffined stopper did not absorb a measurable amount of gas during the experiments.

In the first series of experiments comparatively large pieces of rubber were used and the measurements made at intervals of a minute. In the second series small pieces of the material were allowed to come to equilibrium with the gas by standing 18 hours before the final measurements were made. The results are shown graphically in Figs. 4 and 5.

#### COMPARISON OF RATES OF ABSORPTION OF CHLOROPICRIN AND PHOSGENE

The results of these experiments left no doubt that small concentrations of chloropicrin are absorbed very quickly when exposed to comparatively large rubber or rubberized surfaces. There were some grounds, however, for doubting the ability of rubber to absorb other gases in equivalent amounts. As phosgene was a very important war gas with markedly different properties, it was decided to compare its rate of absorption by rubber with that of chloropicrin. Of course, the physiological method of analysis could not be used, as phosgene is not a lachrymatory gas. It was necessary, therefore, to resort to chemical methods and to use much heavier concentrations of gas.

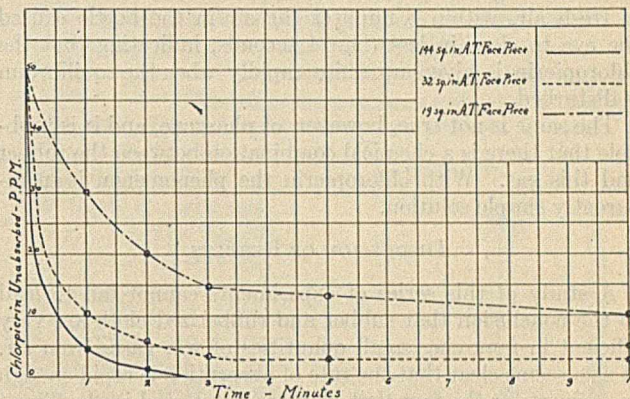


FIG. 4—CURVES SHOWING RATE OF ABSORPTION OF CHLOROPICRIN BY RUBBER FACE-PIECE MATERIAL

**MATERIALS AND APPARATUS**—The material used for the comparison was cut from an original sheet of face-piece rubber before molding. Strips of this material 1 inch wide and 8 inches long were cut, this being a convenient size for the absorption bulb.

The apparatus consisted of the following:

- 1—A tubulated glass bulb of 1-liter capacity used as the absorption chamber.
- 2—A Geissler potash bulb for absorbing and determining the residual gas.
- 3—A 10-liter aspirator bottle for drawing the gas through the absorbing solution.

**METHOD**—The strip of rubber was suspended in the absorption bulb by means of a glass rod and small pieces of wire. A known amount of gas was then put into the bulb by means of a rubber syringe in the case of phosgene, and by a mercury-filled Hempel buret in the case of chloropicrin. The gas was allowed to stand in contact with the rubber for time intervals varying from 15 minutes to 16 hours. At

the end of the selected interval the residual gas was drawn through the absorbing solution and analyzed. Control analyses were made on the apparatus to determine the actual amount of gas being put into the bulb. The results are shown in Fig. 6.

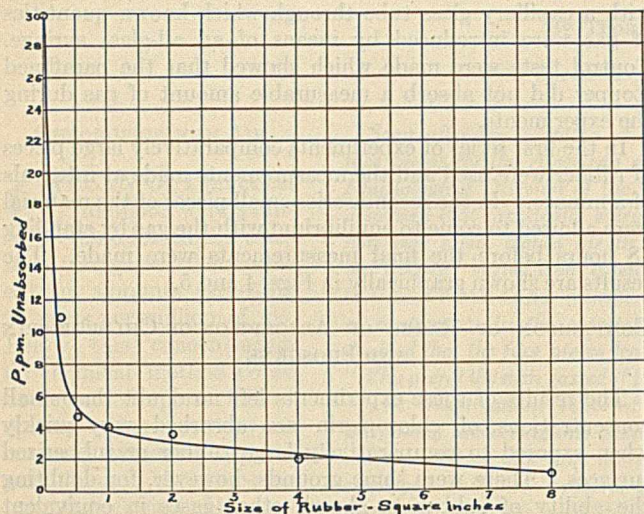


FIG. 5—ABSORPTION OF CHLOROPICRIN BY AKRON TISSOT FACE-PIECE MATERIALS. TIME OF EXPOSURE—18 HOURS

It will be noted that the absorption curves cross at 3 hours' exposure. This indicates that the chloropicrin is absorbed at a faster rate than phosgene, but is also given up at a faster rate when fresh air is drawn into the bulb. When a chloropicrin-containing test piece was dropped into a 500-cc. bottle of fresh air, within 5 minutes the air in the bottle caused the eye to close in less than 4 seconds, indicating that the chloropicrin is given up quite rapidly when the equilibrium is disturbed.

The same is not true, however, of phosgene, and it is probable that there is a chemical combination between the rubber and this gas. With chloropicrin the phenomenon is an apparently simple solution.

#### DISCUSSION OF RESULTS

A study of this series of experiments cannot fail to lead to the conclusion that rubber and rubberized cloth are very efficient in removing small quantities of war gases from air. It also seems clear that the rate of absorption is rapid enough to account for the fact that men are not gassed in the Tissot type masks even when these masks allow several hundred cubic centimeters of gas-laden air per minute to leak in. In the case of a gas that is not soluble in rubber the protective effect of the face piece would not be in evidence. It happens, however, that the three really important gases—phosgene,

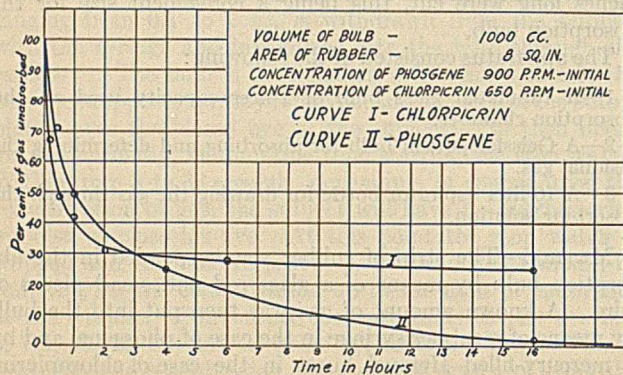


FIG. 6—COMPARISON OF ABSORPTIVE POWER OF RUBBER FOR CHLOROPICRIN AND PHOSGENE

chloropicrin, and mustard gas—are all highly soluble. In fact, practically all the gases suggested for war use that are at all suitable for the purpose are sufficiently soluble in rubber to make the protective effect of the face-piece material well worthy of consideration.

Aside from its relation to war gas problems, the physiological method of gas determination herein described should be of assistance in determining the extent and rate of absorption of many vapors. Data of this kind should be valuable in the study of problems of sanitation, ventilation, hygiene, and occupational diseases.

#### ACKNOWLEDGMENT

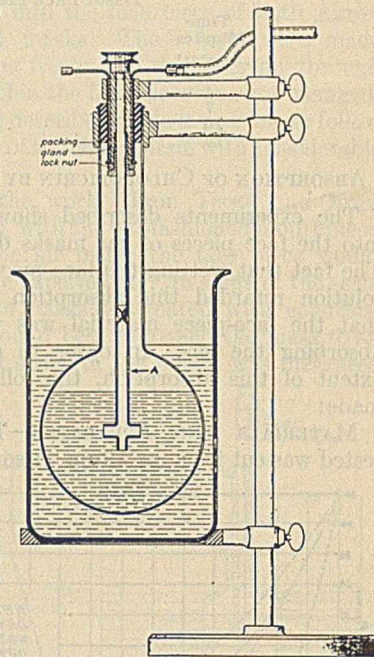
The writer wishes to extend his sincere thanks to R. G. Pierre for his coöperation and suggestions, and to Stanley K. Reimann and Rolland R. Etter for their active assistance.

## A Gas-Tight Stirrer<sup>1</sup>

By George E. Holm and George R. Greenbank

BUREAU OF ANIMAL INDUSTRY, WASHINGTON, D. C.

THE accompanying cut illustrates the principal features of the stirrer. The bearing and the shaft are machined from steel and hardened, and the shaft is then lapped to fit the bearing with the use of fine emery. The construction of the stuffing box is fully explained in the diagram. The packing used may be cotton waste saturated with the same oil as that used for lubrication. Brass inlet and outlet tubes of  $\frac{1}{16}$ -inch diameter are soldered into grooves made in the bearing. Although the apparatus may be constructed in dimensions suitable to the work in which it is to be used, the size found most suitable in laboratory work was of the following dimensions: length of bearing,  $2\frac{1}{4}$  inches; diameter of bearing,  $\frac{5}{8}$  inch; length of shaft, 7 inches; diameter of shaft,  $\frac{1}{4}$  inch; diameter of stuffing box,  $\frac{3}{8}$  inch.



The glass stirrer is fastened to the shaft with litharge-glycerol cement. It is closed to prevent contact of the liquid with the metal shaft, and contains a small hole, A, just above the level of the liquid. Upon rapid stirring, the gas and the liquid is drawn in through the lower end of the stirrer. Both are thrown out through the arms of the stirrer, thus producing a continuous circulation and mixing of the liquid and the gas in the vessel under a constant gas pressure.

The apparatus shown has been used where thorough mixing of a gas and liquid was desired and where it was desired to measure the quantities of gas absorbed by a liquid in successive intervals of time. The stirrer may be run at a high speed for a long time without great wear, and will also permit relatively high vacuum or pressure within the vessel, without danger of gas leakage.

<sup>1</sup> Received September 26, 1923.

# The Effect of Various Pigments upon the Rate of Oxidation of Linseed Oil<sup>1</sup>

By F. H. Rhodes and A. E. Van Wirt

CORNELL UNIVERSITY, ITHACA, N. Y.

IT IS well known that the nature of the pigment present in a paint has a distinct influence upon the rate of drying of the paint and upon the characteristics of the film obtained after drying is complete. For example, the drying is accelerated by white lead and retarded by carbon black, while a paint made from zinc white dries to a harder and more brittle film than does a paint made from white lead. Sabin<sup>2</sup> has shown that the change in weight undergone by a paint film during drying depends upon the nature of the pigment present in the paint; while Gardner<sup>3</sup> points out that the composition of the volatile matter given off during the drying depends upon the pigment used in the paint. Boughton<sup>4</sup> found that the drying of linseed oil is accelerated more by white lead than by zinc white, and more by zinc white than by china clay. Various other investigators have studied this problem of the effect of pigments upon the drying of linseed oil, but the data that have been published upon this subject are more or less fragmentary and sometimes contradictory.

Most of this previous work has been of a qualitative rather than of a quantitative nature. The rates of drying of the paints have been determined by measuring the rates of change in weight of paint films exposed to the air or by noting the times required for the films to become dry to the touch. The change in weight of the film is not an accurate measure of the extent to which the oil has been oxidized, since the oxidation is accompanied by an evolution of volatile matter and the amount and the nature of this volatile matter may vary with the nature of the pigment present in the paint and with the conditions under which the oxidation takes place.<sup>3,5</sup> The time required for the film to become dry to the touch is not a satisfactory criterion of the rate of oxidation of the oil, since, as we shall show, the apparent "dry point" does not always coincide with the same stage in the oxidation. This previous work, therefore, while it may have served to show qualitatively the effect of the nature of the pigment upon the rate of drying of the paint, has afforded little quantitative information as to the effect of the pigment upon the progress of the oxidation of the oil.

## APPARATUS (FIG. 1)

A wide-mouthed suction flask was placed in a thermostat which was kept at 30° C. ( $\pm 0.2^\circ$ ). The mouth of the flask was closed tightly with a rubber stopper. At the bottom of the stopper was a small hook, from which was suspended a frame of copper wire carrying two strips of cloth, each 2 cm. wide and 10 cm. long. To the side arm of the suction flask was attached a capillary glass tube extending to the top

*In the work described in this article an attempt has been made to determine quantitatively the effects of some of the more common white pigments upon the actual rate of oxidation of linseed oil. Films of weighed amounts of paints, prepared from known weights of pigment and linseed oil, were exposed to pure oxygen at constant temperature and pressure, and the rates of absorption of oxygen and of evolution of volatile matter were measured. A number of such experiments were made, using paints prepared from some of the more important and more commonly used white pigments, and the results obtained with the different paints were compared.*

of a mercury-filled Hempel buret. A side arm from this capillary was attached, through a small manometer, with a glass bulb filled with air and immersed in the water within the thermostat. The bottom of the suction flask was covered with a layer of soda lime, and one or more vials of concentrated sulfuric acid were placed within the flask. The soda lime and the sulfuric acid served to absorb the carbon dioxide, water vapor, and volatile organic matter which might be evolved during the drying of the paints and the presence of which might affect the results obtained. The apparatus was placed in a dark corner of the laboratory and the flasks containing the films of paint were, of course, submerged in water, so that practically all light was excluded from the oxidizing films.

## PROCEDURE

The buret was filled with pure oxygen, and oxygen was blown through the flask until all the air was displaced. The cloths on the frame were weighed, coated with enough paint to give an even film without running or segregating, and again weighed. Approximately the same amount of paint (1.8 grams, corresponding to about 0.72 gram of oil) was taken in each experiment, and the sample was spread out to a film of the same area in each case. After the sample was weighed the cloths were suspended in the flask, the flask was rinsed out again with the oxygen, and the stopper was forced firmly into position. The amount of oxygen in the system was adjusted until the buret contained exactly 100 cc. of oxygen when connected with the flask and when the entire system was at atmospheric pressure. The reading on the manometer between the comparison bulb and the capillary tube, and the barometric pressure and the temperature of the buret were noted. At intervals, as the oxygen was absorbed, the level of the mercury in the buret was raised until the manometer was restored to its original reading and the volume and the temperature of the unabsorbed oxygen in the buret were observed. From the readings thus taken the weights of oxygen absorbed during the various intervals of time were calculated. After each reading the system was left standing under a pressure slightly greater than atmospheric, while before each read-

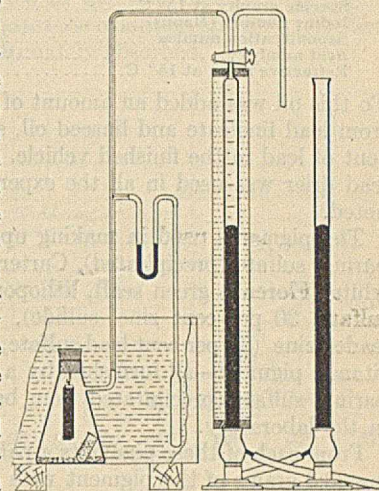


FIG. 1

<sup>1</sup> Received May 2, 1923.

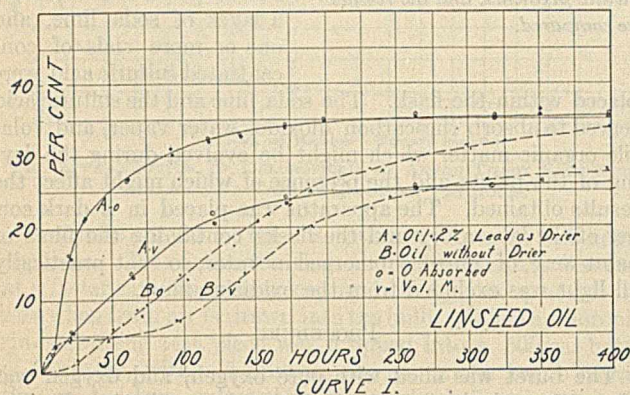
<sup>2</sup> THIS JOURNAL, 3, 81 (1911).

<sup>3</sup> Ibid., 6, 200 (1914).

<sup>4</sup> Bur. Standards, Tech. Paper 71 (1916).

<sup>5</sup> Coffey, J. Chem. Soc. (London), 119, 1152 (1921).

ing the pressure within the system was slightly less than the initial pressure, so that the average pressure was substantially equal to the initial atmospheric pressure. Since the readings were taken at frequent intervals the variations in pressure were so slight as to be negligible. Several times during each run the sample of paint was removed from the flask and weighed. From the data thus obtained the amount of volatile matter—the difference between the actual weight of the sample and the sum of the original weight of the sample plus the weight of the absorbed oxygen—was determined. Whenever the flask was opened to remove the sample for weighing, the entire system was blown out with oxygen to remove any gaseous impurities that might have escaped absorption by the soda lime or the sulfuric acid. No difference was ever observed between the rates of absorption immediately before and immediately after sweeping out the system in this way, so that any unabsorbed volatile matter, if present, had no appreciable effect upon the rate of absorption of oxygen.



MATERIALS USED

The linseed oil used in these experiments showed the following analysis:

Specific gravity at 15° C.....	0.9335
Iodine number (Hanus).....	189
Saponification number.....	196
Acid number.....	0.83
Refractive index at 15° C.....	1.4086

To this oil was added an amount of drier solution, prepared from lead linoleate and linseed oil, sufficient to give 0.2 per cent of lead in the finished vehicle. This oil containing the lead drier was used in all the experiments unless otherwise noted.

The pigments used in making up the paints were: silix, barium sulfate (precipitated), Carter process white lead, zinc white (Florence green seal), lithopone (70 per cent barium sulfate, 30 per cent zinc sulfide), basic sulfate of lead, leaded zinc (25 per cent lead sulfate, 75 per cent zinc oxide), titanox pigment—all furnished by a paint manufacture; and barium sulfate (precipitated from barium chloride) prepared in the laboratory.

From each of these pigments a paint was prepared by mixing 33.3 grams of the pigment with 50 grams of the vehicle (oil containing the lead drier) and grinding the mixture thoroughly to secure uniform incorporation. Each paint was allowed to stand in a tightly sealed container for about 3 weeks before use.

#### RATE OF OXYGEN ABSORPTION BY VEHICLE ALONE

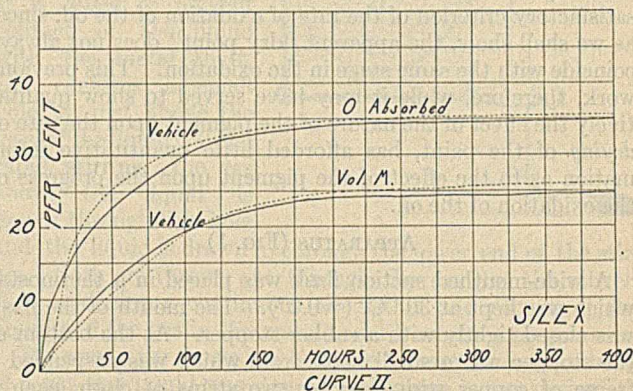
The first experiments were made to determine the rate of absorption of oxygen by the vehicle alone. Two such runs were made in order to find out whether or not the method used would give consistent results. The results of these experiments are shown graphically by Curve I-A in which the amounts of oxygen absorbed by the oil and the amounts of volatile products formed during the oxidation (each expressed in terms of percentage by weight of the original oil)

are plotted against the lengths of time of exposure. The results obtained in the two experiments were in very close agreement. In each case the oil oxidized rapidly at first, but the rate of oxidation decreased progressively and became very slow indeed after about 300 hours. The actual weight of the oxygen absorbed during the period of observation was about 36 per cent of the original weight of the oil.

It will be observed that at the very beginning of the oxidation there was a "period of induction" during which the absorption of oxygen proceeded relatively slowly. This would seem to indicate that the lead linoleate was not the real catalytic agent in the oxidation of the oil—or, at least, that the lead linoleate was not the only catalytic agent which accelerated the drying. Apparently, there was being formed, during this period of induction, some oxidation product which served to promote the union of the oxygen with the oil. These results support the hypothesis, which has been advanced by a number of investigators, that the oxidation of linseed oil is an autocatalytic reaction.<sup>6</sup>

The formation of volatile matter by the oxidation of the oil proceeded rapidly at first, but more slowly as the rate of oxidation decreased. The total amount of volatile matter formed during the period of observation was about 26 per cent of the original weight of the oil.

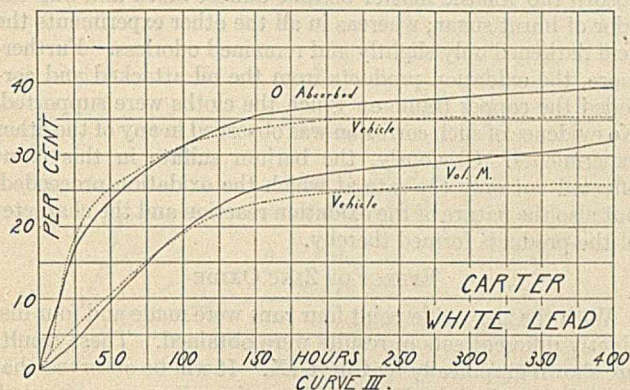
For purposes of comparison, a run was made to determine the rate of oxidation of the linseed oil alone, without drier. The oil used was from the same lot as that used in making the vehicle employed in the experiment described above. The results are shown graphically by Curve I-B. The oxidation of the oil alone proceeded much more slowly than did the oxidation of the oil containing the lead drier. The total amount of oxygen absorbed during the period of observation was somewhat less than the amount taken up by the oil containing the lead linoleate, but from the slopes of the curves it appears probable that the oil alone would ultimately absorb as much oxygen as would the oil made up with the drier. The form of the oxidation curve is rather interesting. During the first 15 hours oxidation took place very slowly. After this "period of induction" the oil absorbed oxygen at an almost uniform rate until about 27 per cent of oxygen had been taken up. The fact that the rate was constant throughout this period instead of decreasing as the oxidation proceeded may indicate that the formation of the autocatalyst was not completed during the first period of induction, but continued throughout at least the early part of the period of oxidation. The break in the oxidation curve at the end of the first 200 hours corresponded with the point at which the oil hardened.



Volatile matter was given off rapidly during the first 20 hours' exposure. The high rate of volatilization during this period may have been due, in part at least, to the simple evaporation of certain volatile compounds present in the oil

<sup>6</sup> Fahrion, *Chem. Ztg.*, **28**, 1196 (1904); Genthe, *Z. angew. Chem.*, **19**, 2087 (1906); Orloff, *J. Russ. Phys.-Chem. Soc.*, **43**, 1509 (1911).

at the beginning of the experiment. Following this first period of rather rapid evaporation, volatile matter was given off slowly at first and then more rapidly until the hardening point of the oil was reached. From this point until the end of the experiment the evolution of volatile matter continued rather slowly. It will be observed that the oil without the drier gave slightly more volatile matter than did the oil to which the drier had been added.



#### SILEX ADDED

The rate of drying of a paint made from silex and the vehicle is shown on Curve II. For purposes of comparison, the curves for the vehicle alone, without pigment, are also shown. In these curves, as in all the curves accompanying this article, the amounts of oxygen absorbed and of volatile matter given off are expressed in terms of percentages by weight of the oil in the sample of paint exposed.

It will be observed that the addition of the silex did not materially affect either the rate of absorption of oxygen or the rate of formation of volatile matter. The slight differences which were produced by the presence of the silex may or may not be significant. Apparently, this pigment accelerated the rate of formation of the autocatalyst and thus shortened the period of induction. After about the fifth hour the rate of oxidation began to decrease slightly, owing possibly to the effect of the silex in increasing the thickness of the film and thus increasing the distance through which the oxygen must diffuse to reach the unoxidized oil. After about the fiftieth hour this effect began to disappear. That silex does not permanently decrease the rate of oxidation may be explained by assuming that in the later stages of the oxidation the actual rate of combination of the oil with oxygen, rather than the rate of diffusion, becomes the controlling factor in determining the rate of reaction; or it may be explained by the hypothesis that the silex tends slightly to delay the hardening of the oil and thus keeps the film somewhat more permeable to oxygen during the later stages of the reaction. After about 110 hours the oxidation curve for the silex paint was substantially identical with the oxidation curve for the vehicle alone. These results indicate that silex has little specific effect upon the rate of oxidation of linseed oil.

#### CARTER WHITE LEAD ADDED

The effect of Carter process white lead is shown by Curve III. In this case, as in the case of the silex, the addition of the pigment increased the thickness of the film and therefore slightly retarded the absorption of oxygen during the earlier stages of drying. Unlike the silex, however, the white lead increased the total amount of oxygen ultimately absorbed by the oil. This drying effect became apparent after about 100 hours' exposure. The total amount of oxygen taken up in 400 hours was about 39 per cent of the weight of the oil, while

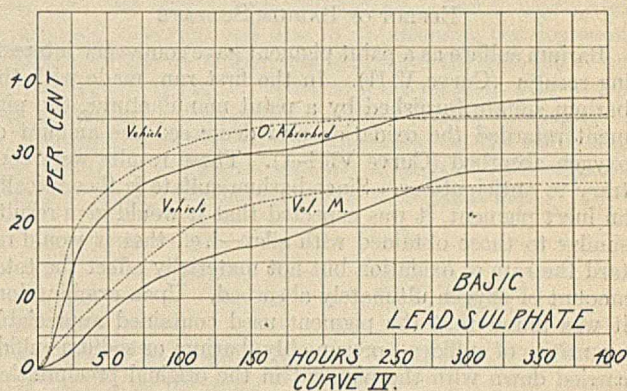
the vehicle alone absorbed only about 36 per cent; the total amount of volatile matter formed was about 32 per cent, while the vehicle without the pigment evolved only about 26 per cent. It is apparent, therefore, that the Carter process white lead does have some effect in increasing the amount of oxygen absorbed by linseed oil, although this effect is not apparent during the earlier stages of the oxidation.

#### EFFECT OF BASIC LEAD SULFATE

Curve IV shows the effect of the basic lead sulfate. This pigment gave results somewhat similar to those obtained with Carter process white lead, but the retarding effect in the earlier stages of the drying was more pronounced and continued for a longer time, while the accelerating effect in the later stages of the oxidation was not so great. The differences between the effects of the two pigments may be due to the smaller particle size and the slighter basicity of the basic sulfate. Being finer than the white lead, the sulfate might be expected to interfere more seriously with the diffusion. The sulfate pigment is less strongly basic than the carbonate white lead, and therefore does not react so readily with the oil to form the lead salts, which tend to act as oxygen carriers and to compensate in part for the delay caused by the slower diffusion.

#### EFFECT OF LITHOPONE

The results obtained with the paint made from lithopone are shown in Curve V. It will be observed that lithopone retards the rate of oxidation and decreases both the amount of oxygen absorbed and the amount of volatile matter given off. The total amount of oxygen absorbed in 400 hours was only 27 per cent of the original weight of the oil; the total amount of volatile matter produced was only 16.4 per cent of the weight of the oil. It is interesting to note that if the effect of the lithopone upon the drying of the oil had been measured simply by determining the change in weight of the film, the results would have led to the very incorrect conclusion that this pigment accelerates the oxidation and does not affect the amount of oxygen ultimately absorbed.



#### EFFECT OF TITANOX PIGMENT

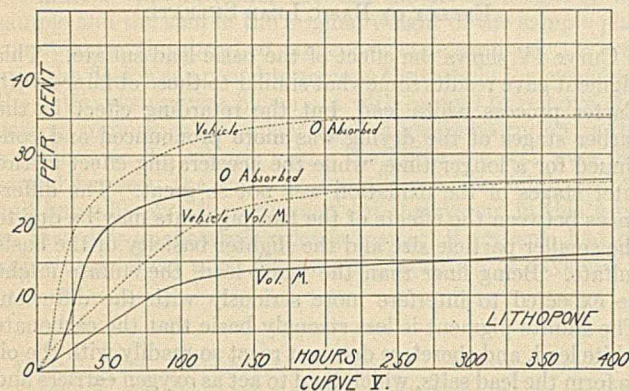
The effect of the titanox pigment, as shown by Curve VI, was very similar to that of the lithopone. The titanox decreased the rate of absorption of oxygen and of evolution of volatile matter, and decreased the amount of oxygen absorbed and the amount of volatile matter given off.

#### EFFECT OF LEADED ZINC PIGMENT

The behavior of the paints made from the leaded zinc pigment is shown by Curve VII. With these paints two runs were made. In each case the paint absorbed oxygen more slowly than did the vehicle alone, and the amount of oxygen

taken up and the amount of volatile matter given off were much smaller than in the case of the vehicle without pigment.

In the first experiment (Curve VII-A) the absorption of oxygen took place rapidly during the first 55 hours and then stopped. Volatile matter was given off rapidly at first, but slowly after the fifty-fifth hour. The breaks in the two curves occurred simultaneously with the setting of the paint.



In the second experiment (Curve VII-B) the paint began to set in about 40 hours, but the setting and hardening were not complete until about the end of 110 hours. The total amount of oxygen taken up was the same as in the first run. Because of the fact that the film did not harden so quickly but remained permeable for a somewhat longer time, more volatile matter was given off in the second run than in the first.

A certain similarity may be observed in the behavior of the paints made from lithopone, titanox, and leaded zinc. In each case the pigment retards the absorption of oxygen and the evolution of volatile matter and decreases the amount of oxygen ultimately absorbed and the amount of volatile matter ultimately given off. This decrease in the rate and extent of oxidation does not necessarily increase the time required for the paint to become dry, since some of these pigments cause the paint to set and harden at an early stage in the oxidation.

#### EFFECT OF BARIUM SULFATE

Barium sulfate as a paint pigment gave some very interesting results (Curve VIII). In the first run, made with the barium sulfate furnished by a paint manufacturer, the pigment retarded the oxidation and decreased the amount of oxygen absorbed (Curve VIII-A). These results were contrary to anticipations. Since barium sulfate is theoretically an inert pigment, it was expected that it would give results similar to those obtained with silix—i. e., that it would retard the rate of oxidation but not materially affect the total amount of oxygen ultimately absorbed. Upon examination, it was found that the pigment used contained appreciable quantities of sulfides—presumably, barium or sodium sulfide carried down with the pigment in the original precipitation and not removed by the subsequent washing. The unexpected behavior of the paint made with this pigment may have been due to the presence of this sulfide.

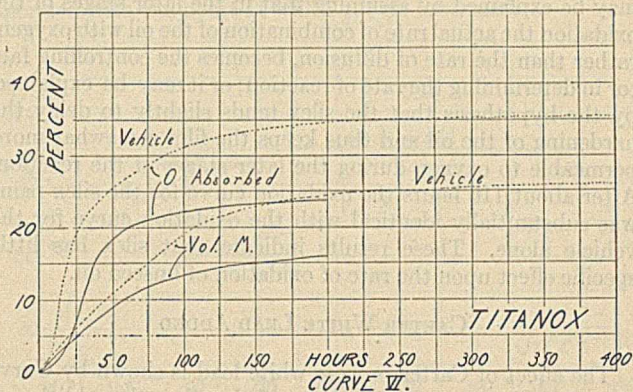
A sample of barium sulfate was prepared in the laboratory by adding an excess of a dilute solution of barium chloride to dilute sulfuric acid and washing and drying the resulting precipitate. This pigment was, of course, free from sulfides, but it did contain a small amount of adsorbed barium chloride. With a paint made from this pigment two runs were made. The results obtained were practically identical, and are shown by Curve VIII-B. The barium sulfate made in the laboratory, like the commercial product, retarded the oxidation in the initial stages of the reaction and decreased the total amount of oxygen taken up, although its effect in cutting

down the amount of oxidation was not so pronounced. The amount of volatile matter was very greatly increased and was always greater than the amount of oxygen absorbed, so that the film of paint decreased in weight continuously from the beginning to the end of the period of exposure. The amount of volatile matter given off was more than half the weight of the oil in the original film, and the final film was very thin and dry. The sulfuric acid placed in the reaction chamber to absorb the volatile matter became almost black and had the odor of burnt sugar; whereas in all the other experiments the acid darkened only slightly and remained odorless. Furthermore, the oxidation products from the oil attacked and corroded the copper frame on which the cloths were supported. No evidence of such corrosion was observed in any of the other experiments. Obviously, the barium sulfate in this paint affected not only the rate at which the oxidation proceeded, but also the nature of the oxidation reaction and the character of the products formed thereby.

#### EFFECT OF ZINC OXIDE

With the zinc oxide paint four runs were made and four distinctly different sets of results were obtained. These results are shown graphically by Curve IX. It will be observed that in each case the initial rate of absorption of oxygen was much lower than the rate of absorption by the vehicle without pigment. This might be expected, since zinc oxide is a very finely divided pigment and should tend greatly to reduce the rate of diffusion of oxygen into the oil. It will also be noted that in each case the total amount of oxygen absorbed during the period of observation was less than the amount absorbed by the free vehicle in similar time, and that the amount of volatile matter given off was less than the amount evolved by the vehicle alone under similar conditions.

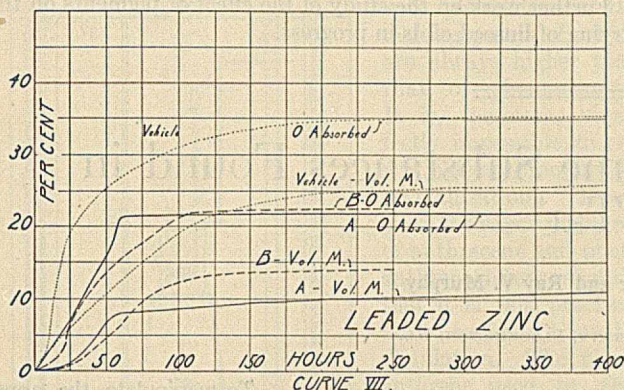
In the first experiment (Curve IX-A) the absorption of oxygen took place uniformly and fairly rapidly during the first 120 hours and very much more slowly thereafter. The rate of evolution of volatile matter was very slow at first, but increased rapidly during the first 120 hours. At the end of this time there was a sharp break in the volatile matter curve, and during the latter part of the run volatile matter was given off slowly and at a fairly uniform rate. The form of the curve during the earlier stages of drying suggests that the oxidation of linseed oil may, under certain conditions, proceed in a number of more or less consecutive stages, and that the production of volatile matter is less rapid during the primary stages of the oxidation.



In the second experiment (Curve IX-B) the initial oxidation took place somewhat more rapidly, although not so rapidly as in the case of the vehicle alone. The paint began to harden after about 40 hours' exposure, and was hard at the end of 90 hours. The curve for the evolution of volatile matter showed neither the rapid rise nor the abrupt break that were observed in the first run. In this second experiment the paint

began to set before the reaction, which is responsible for the formation of most of the volatile matter, could proceed to any considerable extent.

In the third run (Curve IX-C) the rate of oxidation during the early part of the reaction was identical with that in the second experiment. The setting occurred suddenly, however, after about 40 hours' exposure. It will be noted that the break in the oxidation curve at this point is very abrupt.



In the fourth experiment (Curve IX-D) the rate of oxidation during the first 40 hours was the same as that in the second and the third runs. Setting took place suddenly at the end of the fortieth hour. Apparently, the film obtained by the setting of this sample was very much less pervious than the hardened film in the third experiment, since very little oxygen was absorbed and very little volatile matter was produced after setting occurred. In this last experiment, the paint made from zinc white gave results very similar to those obtained in the first run with the paint containing leaded zinc.

In the case of the zinc oxide paint, therefore, four samples gave four different types of results. The differences in the results may be explained by the fact that the various samples set and hardened at different rates and at different stages in the oxidation, and gave films of different hardnesses and permeabilities. In the first run setting took place rather gradually, but after about 125 hours the set film underwent a sudden hardening that markedly decreased its permeability; in the second experiment the setting and hardening took place at an earlier stage in the oxidation, but less suddenly; in the third and fourth runs setting and hardening were practically simultaneous and took place suddenly, but the hardened films differed in permeability. There is no apparent reason for the fact that four samples of the same paint, when exposed under as nearly as possible identical conditions, set and hardened at different stages in the oxidation and formed films of different permeabilities.

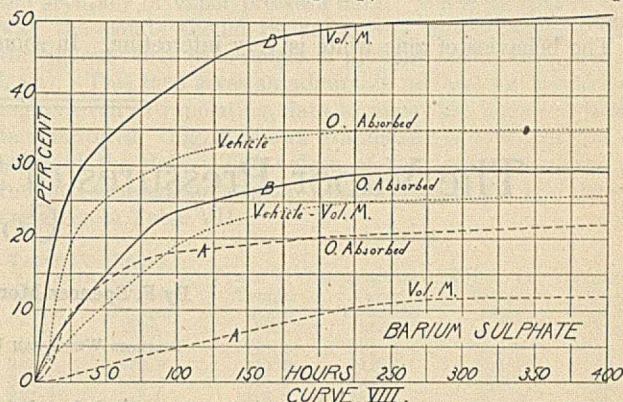
#### CONCLUSIONS

Evidence has been secured in support of the hypothesis that the drying of linseed oil is an autocatalytic reaction. The real catalyst is an oxidation product of the oil itself. The well-known effect of lead salts in accelerating the drying of the oil is due to the fact that these salts act as pseudo-catalysts to promote the formation of the autocatalysts and thus increase the rate of oxidation when the oil is first exposed to the air. The lead drier does not appear to have any marked effect upon the total amount of oxygen ultimately absorbed by the oil in drying.

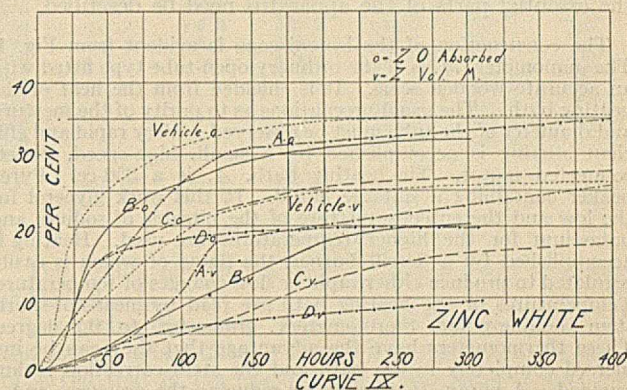
The addition of a pigment to the oil may have a marked effect upon the rate of absorption of oxygen and the rate of evolution of volatile matter, and upon the amount of oxygen absorbed and the amount of volatile matter given off. Upon the basis of their effects upon the oxidation of linseed oil we may distinguish several more or less separate groups of pigments.

The pigments of the first group, of which silicic acid is an example, have little or no effect on the oxidation other than that due to the fact that they increase the thickness of the film and thus decrease the rate of diffusion of oxygen into the oil. Such pigments retard the oxidation, but do not appreciably alter the amount of oxygen ultimately absorbed or the amount of volatile matter ultimately evolved.

The pigments of the second group, which includes such ap-



parently dissimilar substances as leaded zinc, lithopone, titanox, and barium sulfate contaminated with a small amount of sulfides, slow down the oxidation and the evolution of volatile matter and materially decrease the amount of oxygen absorbed and the amount of volatile matter given off. Such pigments appear to owe their effects, in part at least, to the fact that they cause the oil to harden at an earlier stage in the oxidation than does linseed oil without pigment. Such pigments may or may not shorten the apparent drying time. If the pigment greatly decreases the initial rate of oxidation or if it has comparatively little effect in accelerating gelatinization, the drying time may be increased; if the pigment greatly accelerates gelatinization or if it only slightly retards oxidation, it may shorten the time required for the paint to set and dry. It is to be expected that such pigments may affect the character of the paint film—the hardness, brittleness, etc.—not only by their mechanical action as aggregates in the paint concrete, but also by determining the degree of oxidation of the oil in the hardened film, the amount of oil lost by the formation of vapors, and the rapidity with which the solidification of the oil proceeds. Future investigation of the exact effects of various substances on the hardening of linseed oil may afford information which will enable us more closely to control the characteristics of the paint films.



The third group of paint pigments includes those which tend to increase the amount of oxygen absorbed by the oil and the amount of volatile matter given off. This group includes such pigments as Carter white lead and basic lead sulfate. These substances generally tend to retard the initial oxidation,

the retardation being due, presumably, to the fact that the pigment interferes somewhat with the diffusion of the oxygen into the film. During the latter stages of the oxidation the pigment acts as a drier to increase the amount of oxygen absorbed by the oil. The very fine and only slightly basic sublimed white lead more markedly retarded the initial oxidation and less markedly accelerated the final oxidation than did the coarser and more strongly basic Carter process white lead.

The behavior of zinc white is very interesting. In some

cases this pigment acts as an inert pigment like silicic acid—it decreases the initial rate of oxidation but does not materially decrease the amount of oxygen ultimately taken up or the amount of oxygen ultimately evolved. In other cases the zinc oxide behaves like lithopone or leaded zinc in that it causes the oil to harden at an early stage in the oxidation and thus decreases the amount of oxygen absorbed and the amount of vapors given off.

Further work on the study of the effect of pigments on the drying of linseed oil is in progress.

## The Vapor Pressures of Some Substances Found in Coal Tar<sup>1</sup>

By F. Spencer Mortimer and Ray V. Murphy

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THE purposes of this article are (1) to describe a simple yet reliable method for the measurement of vapor pressures of organic compounds, and (2) to present the results of measurements upon some commercially important substances found in coal tar—viz., carbazol, phenanthrene, anthracene, fluorene, acenaphthene, and naphthalene.

Smith and Menzies<sup>2</sup> have reviewed the principles underlying the exact measurement of vapor pressures, and more recently Nelson and Senseman<sup>3</sup> have given a brief but excellent summary of the literature relative to these particular substances. It is manifestly unnecessary to further survey the history of the subject at this time.

### THE APPARATUS AND ITS MANIPULATION

The apparatus employed for measuring the vapor pressures is a modification of the static isoteniscope method described by Smith and Menzies.<sup>2</sup> (Fig. 1) It is simple in design and is constructed of such materials as are commonly found around laboratories of moderate means. Only the essential parts of the apparatus need be described.

The construction of the isoteniscope is evident from Fig. 1. The manometer, *M*, is of the ordinary open-tube type fitted with an accurate wooden scale. It is shielded from the heat of the heating bath. The usual precautions as to purity of the mercury and diameter of the tube must be observed. Very rapid and efficient stirring is accomplished by a small, high-speed, direct-connected motor. The heating bath, *A*, is a 250-cc. Pyrex beaker containing a suitable liquid. In this work glycerol for the low and the eutectic mixture of the nitrates of sodium and potassium for the higher temperatures are used. Heating is accomplished by a Tirrill burner, the flame of which is easily regulated to produce either rapid or slow changes of temperature. Temperatures of the heating bath are read by means of short-stem boiling-point thermometers graduated to 0.2 degree. These thermometers have the advantage that they can be immersed completely in the bath and the stem correction is thus avoided. A pump, *H*, is used for reducing the pressures and a 20-liter bottle, *G*, serves as reservoir. The complete apparatus is set up as a single unit on a small table fitted with two rigid uprights and crossbar as shown in the diagram.

*A simple method for determining vapor pressures of organic compounds has been described.*

*The vapor pressures of naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, and carbazol have been determined and the results compared with other published data.*

*The latent heats of vaporization, the sublimation pressures of anthracene and carbazol, and the heats of sublimation have been calculated.*

To manipulate the apparatus, the bulb of the isoteniscope is cut off from the U-tube and charged with such an amount of the material to be studied that, when melted, it will about half fill the bulb and the U-tube to some distance below the two smaller bulbs. It is then resealed to the U-tube and clamped into position. The pressure in the closed system is brought to the highest value to be observed by pumping in air through the stopcock, *I*, or by diminishing the pressure by means of the pump. The temperature of the bath is then raised until the liquid in the isoteniscope boils freely, *C*<sub>1</sub> being open. After the liquid has boiled for about 1 minute to drive out gases and volatile impurities and furnish sufficient liquid for the U-tube, the temperature is permitted to fall slowly at a rate not to exceed 0.2 degree per minute at the higher temperatures or 0.5 degree at the lower pressures. Eventually, a temperature is reached at which ebullition ceases and the level of the liquid in the arm of the U-tube joining *B* begins to fall. When the levels in the two arms of the U-tube are equal, *C*<sub>1</sub> is closed and the temperature of the bath is read. The difference between the levels of the mercury in the manometer is then noted. The algebraic sum of this reading, after correction, and the corrected atmospheric pressure is the vapor pressure at the temperature observed. *C*<sub>1</sub> is again opened, the temperature raised, and the boiling-out process repeated, followed by a repetition of the readings as just outlined. A sufficient number of checks are thus made to insure the accuracy of the results. For the next measurement the pressure is slowly diminished until the liquid again boils at a somewhat lower temperature, after which the process described above is repeated, checking each reading after a second or third boiling of the liquid.

It has been found advisable to adopt this procedure in place of that more commonly used in which the liquid in the isoteniscope is brought to constant temperature and the external pressure adjusted to equal the vapor pressure of the liquid. The procedure described above is more rapid and for this apparatus, at least, is more accurate.

The use of thermometers instead of thermocouples and the noninsulated, gas-heated bath instead of the more elaborate electrically heated types may be criticized. The writers believe, however, that, judging from the log *P* against 1/*T* curves (Fig. 2) the data obtained with this apparatus are at least as accurate as those obtained with the more refined type used by Nelson and Senseman.<sup>3</sup>

### PURIFICATION OF MATERIALS

The starting material for each of the substances used in this work consisted of fairly high-grade products. The

<sup>1</sup> Received May 7, 1923.

<sup>2</sup> *J. Am. Chem. Soc.*, **32**, 1412 (1910).

<sup>3</sup> *THIS JOURNAL*, **14**, 58 (1922).



carbazol and anthracene were each repeatedly recrystallized from chlorobenzene until the melting points were 245.3° and 216.6° C., respectively. In the case of carbazol the nitrogen content indicated a purity of over 99.0 per cent.

Two of the most important impurities in phenanthrene are anthracene and carbazol. Pascal<sup>1</sup> has observed that each of

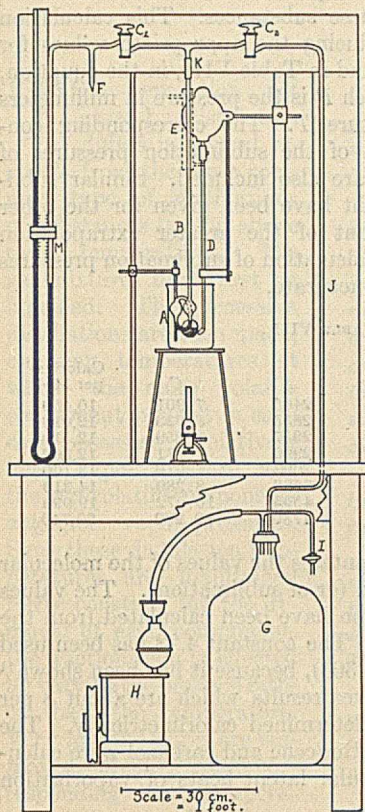


FIG. 1

these substances forms a series of mixed crystals with phenanthrene, the melting points of which are always higher than that of phenanthrene. It is, therefore, manifestly impossible to purify phenanthrene by recrystallization. Moreover, the vapor pressures of anthracene and phenanthrene differ so slightly that it is not practicable to separate them by distillation. The phenanthrene used in this investigation was purified by first redistilling the sample followed by a partial oxidation with chromic acid and acetic acid. The anthracene is more readily oxidized than phenanthrene. The anthraquinone thus formed was removed first by reducing to anthranol with zinc and caustic soda and then washing the product. The phenanthrene was extracted

with benzene and recovered by evaporating to dryness. The product was recrystallized once from alcohol and finally distilled. The middle fraction of this distillate melted at 98.0° C. The methods employed for the purification of the naphthalene, fluorene, and acenaphthene were similar in that each was repeatedly distilled or sublimed and recrystallized until the melting points were constant, as follows: naphthalene 80.1° C., fluorene 114.2° C., acenaphthene 94.1° C.

TABLE I—NAPHTHALENE

Temperature ° C.	Vapor Pressure Mm.
224.1	881.0
223.9	879.7
223.8	878.5
216.4	737.6
216.45	737.6
202.2	520.0
202.2	519.0
202.1	518.5
189.6	376.2
189.6	376.1
178.0	275.2
177.3	269.7
163.9	181.8
160.9	168.1
149.7	117.9
148.7	114.5
147.8	111.4
132.6	67.0
131.1	63.2
130.25	61.2
127.7	50.1
113.0	32.2
98.1	18.3
87.4	11.9
87.2	11.4

TABLE II—ACENAPHTHENE

Temperature ° C.	Vapor Pressure Mm.
287.8	943.0
287.0	932.3
286.8	930.3
275.4	733.4
275.4	733.4
275.3	733.4
264.4	573.5
264.4	573.1
252.5	434.7
252.4	434.5
247.0	382.9
246.6	377.9
246.2	374.6
233.2	272.0
227.2	234.6
210.4	149.0
210.2	148.0
182.4	63.6
182.4	63.6
147.2	19.2

TABLE III—FLUORENE

Temperature ° C.	Vapor Pressure Mm.
300.4	812.3
299.8	804.3
295.7	738.8
295.7	738.8
295.6	738.8
277.1	490.7
276.6	487.5
241.4	208.4
240.4	205.5
203.0	70.5
202.5	69.5
161.0	18.0

DATA OBTAINED

The data obtained are shown in Tables I to VI. These experimental values were then plotted on large-scale coordinate paper (50 x 80 cm.) using the common logarithm of the vapor pressure in millimeters of mercury and the reciprocal of the absolute temperature as the coordinates. This method of plotting furnishes a very useful scheme for judging the accuracy of vapor pressure data. When plotted in this way the points should lie on a very nearly straight line throughout fairly wide ranges of pressure (10 to 1000 mm. at least). This then gives an admirable method for interpolating, or even extrapolating, data to somewhat higher or lower temperatures. Fig. 2 shows graphically a reproduction of some of the data. The values of the vapor pressures at rounded temperatures taken from the log P vs. 1/T curves are given in Table VII.

TABLE IV—PHENANTHRENE

Temperature ° C.	Vapor Pressure Mm.
346.8	883.9
345.7	870.9
345.1	864.4
337.1	741.0
337.1	741.0
325.4	592.6
324.9	588.7
324.5	584.7
306.5	399.7
306.4	399.2
293.2	299.9
293.2	299.8
293.1	299.7
271.5	183.0
271.5	182.9
246.1	94.6
246.0	94.3
233.8	67.5
203.6	27.2

TABLE V—ANTHRACENE

Temperature ° C.	Vapor Pressure Mm.
340.5	742.2
340.5	742.2
340.6	742.2
328.0	584.0
327.9	583.4
327.4	577.4
313.4	437.0
313.2	436.2
312.8	432.9
300.6	334.2
300.0	331.3
299.9	330.4
282.1	219.8
282.0	219.6
260.3	130.2
259.8	128.3
259.4	127.3
244.6	86.5
244.4	85.9
228.0	55.0
223.2	48.0

TABLE VI—CARBAZOL

Temperature ° C.	Vapor Pressure Mm.
351.8	744.0
351.9	744.0
352.0	744.0
337.5	551.6
336.9	547.4
336.8	543.7
309.0	298.0
308.3	295.8
290.6	193.1
290.0	190.5
289.6	187.9
267.3	105.1
266.6	104.5
266.2	103.6
252.5	70.3
252.6	70.3
252.4	70.0
244.8	55.4
244.8	55.0

TABLE VII—VAPOR PRESSURES IN MILLIMETERS OF MERCURY, SMOOTHED RESULTS

Temp. ° C.	Naphthalene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Carbazol
80	9.6	.....	.....	.....	.....	.....
90	13.0	.....	.....	.....	.....	.....
100	19.7	.....	.....	.....	0.045	.....
110	29.3	.....	.....	.....	0.095	.....
120	42.9	.....	.....	.....	0.19	.....
130	61.2	.....	.....	.....	0.38	.....
140	86.0	14.7	.....	.....	0.73	.....
150	119.0	21.4	11.9	.....	1.36	.....
160	162.0	30.5	17.4	.....	2.40	.....
170	218.5	43.0	24.9	.....	4.10	.....
180	290.0	59.3	34.8	.....	6.96	.....
190	378.5	81.4	48.1	.....	11.5	.....
200	490.0	109.0	65.4	24.6	18.6	7.45
210	630.0	146.0	88.6	33.6	29.2	12.1
220	798.0	192.0	120.4	45.4	43.5	18.9
230	.....	250.0	155.0	60.5	58.1	30.0
240	.....	323.5	202.0	80.4	77.2	45.1
250	.....	410.0	259.5	104.5	100.0	65.5
260	.....	520.0	332.0	136.0	129.1	87.3
270	.....	650.0	419.0	174.0	165.5	113.5
280	.....	808.0	527.0	220.0	210.0	147.0
290	.....	998.0	656.0	279.5	265.0	189.0
300	.....	.....	808.0	347.5	331.0	215.0
310	.....	.....	.....	432.0	409.0	305.5
320	.....	.....	.....	531.0	501.0	382.5
330	.....	.....	.....	648.0	610.0	476.0
340	.....	.....	.....	785.0	738.0	586.0
350	.....	.....	.....	946.0	888.0	718.0
Boiling point, ° C.	218.0	277.3	298.0	338.5	342.0	353.0

DISCUSSION OF RESULTS

The results obtained may now be compared with other published data.

Comparing the results shown in the foregoing tables with the corresponding data of Nelson and Senseman,<sup>3</sup> it will be observed that in the case of anthracene there is very close agreement. The experimental data of these investigators for anthracene are not shown in Fig. 2 because of the possibility of confusion with those for phenanthrene. It was observed, however, that both sets of data, when plotted as described above, gave points which were found to lie very nearly on the same straight line.

<sup>1</sup> Bull. soc. chim., 29, 644 (1921).

In the case of phenanthrene and naphthalene the results given here are often very different from those obtained by Nelson and Senseman. Inspection of Fig. 2 indicates that, judging from the standpoint of the  $\log P$  vs.  $1/T$  curves, the data of Nelson and Senseman are somewhat in error for these substances. In the case of phenanthrene this may be due to the use of an impure product. The melting point of the phenanthrene used by them was  $100.0^\circ\text{C}$ . This, calculated from the melting point curve (unpublished data), is equivalent to at least 5 per cent of anthracene, the presence of which would tend to raise the boiling point and lower the vapor pressure.

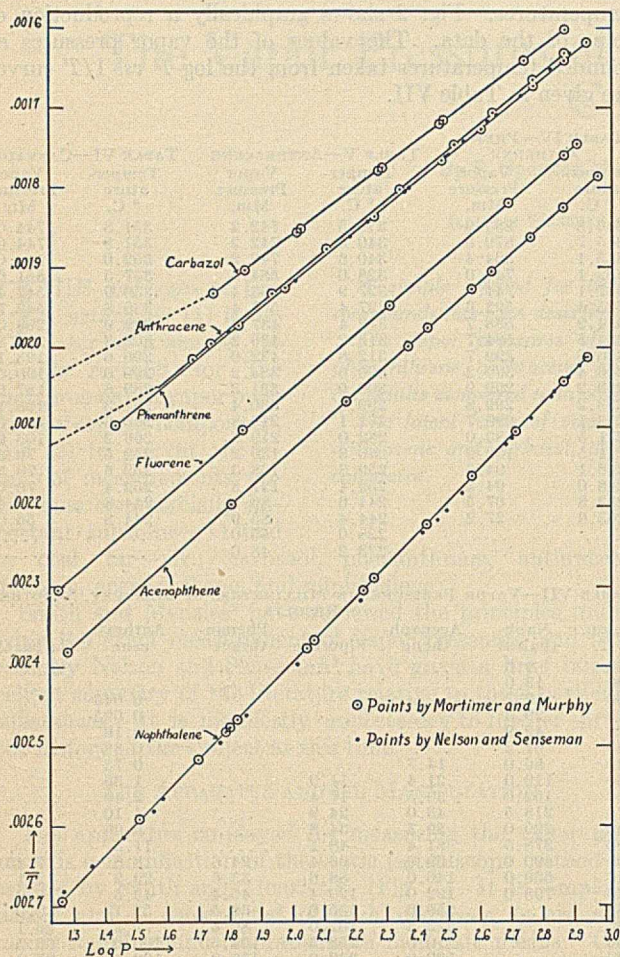


FIG. 2.

The presence of impurities, however, will not account for the differences in the case of naphthalene. It is the opinion of the writers that the method used by Nelson and Senseman is at fault, at least for substances which may decompose, in one particular. The heating bath used by them was arranged to give very slow cooling. The writers have found that if cooling takes place too slowly there may be sufficient decomposition of these substances, after the confining liquid stops boiling and before equilibrium is reached, to cause appreciable differences in the measured pressure. At temperatures near the boiling point, equilibrium is reached more quickly and the two sets of data are in fair agreement, the observed boiling points being identical for naphthalene.

Apparently, no measurements of the vapor pressures of acenaphthene, fluorene, and carbazol<sup>5</sup> are given in the literature. The following points have been recorded, and are

<sup>5</sup> Since this paper was written Senseman and Nelson, *THIS JOURNAL*, 15, 382 (1923), have published data on this substance. The boiling point is found by the authors to be  $353^\circ\text{C}$ .; Senseman and Nelson obtained  $354.76^\circ\text{C}$ .

given here for comparison: carbazol,  $338.0^6$  and  $351.5^7$ ; fluorene,  $305.0^8$  and  $295.0^9$ ; acenaphthene,  $277.5^{10}$

In a recent article Mortimer<sup>11</sup> reviewed the principles relating the vapor pressures and sublimation pressures with the heats of vaporization, sublimation, and fusion. The data given in Table VIII are pertinent to the calculation of the vapor pressures of these substances. This calculation is accomplished by introducing the appropriate values for the constants  $C$  and  $S$ , found in Table VIII, in the equation,  $\log P = C - S/T$ , in which  $P$  is the pressure in millimeters at the absolute temperature  $T$ . The corresponding constants for the calculation of the sublimation pressures of anthracene and carbazol are also included. Similar sublimation pressure data might have been given for the other substances, but on account of the greater extrapolation (lower melting point) the calculation of sublimation pressures for these substances is less accurate.

TABLE VIII

SUBSTANCE	Absolute Boiling Point	$S$	$C$	Calories per Mol
Naphthalene	491.0	2465	7.901	10,450
Acenaphthene	550.3	2835	8.033	12,010
Fluorene	571.0	2957	8.059	12,510
Phenanthrene	611.5	2990	7.771	12,680
Anthracene	615.0	3093	7.910	13,100
Carbazol	626	3380	8.280	14,310
Anthracene (solid)	....	4595	10.972	19,990
Carbazol (solid)	....	4780	10.982	20,710

Column 5, Table VIII, contains the values of the molecular latent heats of vaporization (or of sublimation). The values for the heats of vaporization have been calculated from the expression  $L = 4.23 \times S$ . The constant 4.23 has been used instead of 4.58 ( $1.9885 \times 2.303$ ), because it has been shown<sup>11</sup> that the constant 4.58 gives results which are about 8 per cent greater than those determined calorimetrically. The heats of sublimation for anthracene and carbazol were calculated by adding the molecular latent heats of vaporization and of fusion.

Finally, a comparison of the calculated sublimation pressures of anthracene may be made with the experimental results given by Niederschulte.<sup>12</sup> It was found that the experimental points given by this observer fell quite closely to the calculated  $\log P$  vs.  $1/T$  curve, the deviations being both positive and negative. These calculated sublimation pressures are included in Table VII.

Stelzner<sup>13</sup> has also determined the pressures of anthracene at temperatures below the melting point. Access was not had to the original article, but it is quite evident that the determinations were made on a solution of anthracene rather than on the solid, because the data fall upon the extrapolated vapor pressure curve rather than upon the sublimation pressure curve.

<sup>6</sup> Graebe and Glaser, *Ber.*, 5, 12 (1872).

<sup>7</sup> Chemical Rubber Handbook, 1920, p. 161.

<sup>8</sup> Barbier, *Ann. chim. phys.* [5], 7, 479 (1876).

<sup>9</sup> Chemical Rubber Handbook, 1920, p. 185.

<sup>10</sup> Behr and van Dorp, *Ann. Chem. Pharm.*, 172, 263 (1874).

<sup>11</sup> *J. Am. Chem. Soc.*, 44, 1429 (1922).

<sup>12</sup> Landolt and Börnstein, *Tabellen*, 1912, p. 394; Dissertation, Erlangen, 1903.

<sup>13</sup> Landolt and Börnstein, *Tabellen*, 1912, p. 394; Dissertation, Erlangen, 1901.

### Dr. Sosman Honored

R. B. Sosman, of the Geophysical Laboratory, has been appointed by the National Research Council as American Member on the Permanent Committee for the Standardization of Physico-Chemical Symbols of the International Union of Pure and Applied Chemistry. The other members of the committee are: Ernst Cohen, University of Utrecht, chairman; Alexander Findlay, University of Aberdeen; and Charles Marie, Sorbonne.

# An Improved Method for the Separation of Gas Mixtures<sup>1</sup>

By Fractional Distillation at Low Temperatures and Pressures

By Martin Shepherd and Frank Porter

BUREAU OF MINES, WASHINGTON, D. C.

THE separation of gases by distillation differs in several respects from the more common type of distillations of substances boiling above room temperatures. The gas mixtures must first be liquefied. The successive distillations are then made, choosing temperatures at which the more volatile component present in each case possesses a relatively high vapor pressure, and the less volatile components negligible vapor pressures. Since these distillation temperatures are maintained fairly constant for the removal of each component, the fractionation is effected by varying the pressure rather than the temperature. Very low pressures are employed, which involve corresponding low temperatures. Two decided advantages accrue from these conditions. The first, and by far the most important, is that the ratio of the vapor pressure of the more volatile component to that of the less volatile components becomes very much greater at the lower temperatures, and so the separation is distinctly sharper. The second lies in the fact that the actual amount of the vapor phase over the liquid phase is quite small at the low pressures, and consequently a negligible amount of the vapor phase remains above the liquid at the completion of each distillation—an important consideration where small amounts of gas are used.

## PREVIOUS APPLICATIONS OF FRACTIONAL DISTILLATION

Ramsay,<sup>2</sup> in his memorable work on the rare gases of the atmosphere, used fractional distillation in the separation of the gas mixtures, and was able not only to obtain the gases in a high state of purity, but also to make very accurate analytical separations.

Adaptations of this method have been used by numerous investigators in the preparation of pure gases and the separation of gas mixtures.<sup>3</sup>

<sup>1</sup> Received July 29, 1922. Published by permission of the Director, U. S. Bureau of Mines.

<sup>2</sup> Travers, "Experimental Study of Gases," 1901, p. 212; Ramsay and Travers, *Proc. Roy. Soc. (London)*, **63**, 438; **64**, 183; *Phil. Trans.*, **197**, 47 (1901).

<sup>3</sup> Ab-der-Halden, *J. Gas Lighting*, **126**, 342 (1914); Anderson, *THIS JOURNAL*, **9**, 142 (1917); Anon., *C. A.*, **11**, 296 (1917); Anon., *Gas World*, **59**, 152 (1913); Bordan and Taplav, *Compt. rend.*, **146**, 628; **147**, 591 (1908); Burrell and Robertson, *THIS JOURNAL*, **7**, 209 (1917); *Proc. Am. Gas Inst.*, **9**, 219 (1914); Burrell, Seibert, and Robertson, *Bur. Mines, Tech. Paper 142* (1916); *Ibid.*, **104** (1915); Czoko, *J. Gasbel.*, **56**, 1172 (1913); Erdmann and Stoltzenberg, *Ber.*, **43**, 1702 (1910); Lebeau and Damiens, *Compt. rend.*, **156**, 144, 325, 797 (1913); *J. Soc. Chem. Ind.*, **32**, 126 (1913); *J. Gas Lighting*, **125**, 105 (1913); Stoltzenberg, *Ber.*, **43**, 1708 (1910); Travers, "Study of Gases," p. 210; Whiton, *THIS JOURNAL*, **8**, 733 (1918).

*This paper describes an improved method for the separation of gas mixtures by fractional distillation at low temperatures and pressures. The work was mainly carried out at the Chemical Laboratory, U. S. Helium Plant No. 3, Petrolia, Texas (1920-21).*

*The method, with suitable modifications, is applicable to many problems of gas separation, and may be employed in a great number of cases where ordinary chemical methods do not give results of sufficient accuracy or cannot be used at all. It may be used in technical work, giving results commensurate with the requirements of engineering calculations. With no modifications other than an increase in the number of fractionations resorted to, it may be employed in precision work, either for the preparation of gases of high purity suitable for the measurement of physical constants, or to effect the exact analytical separation of complex mixtures.*

*The method is capable of yielding results of greater accuracy than those obtained by previous distillation methods, and attains this end in a small fraction of the time formerly required.*

*In developing the subject, the general principles of the separation of gases by liquefaction and subsequent distillation are first given; then an account of previous applications, followed by the expression of the need of an improved method, and its development in detail. Illustration is made of the separation of a complex gas mixture containing helium, nitrogen, and the saturated hydrocarbon vapors, and the accuracy of the method set forth. Finally, its application to the preparation of pure gases is described, and the tests of purity of the gases are given.*

Burrell, Seibert, and Robertson<sup>4</sup> were able, by a method similar to that used by Ramsay, to separate analytically the constituents of natural gas.

A brief description of the apparatus and method used by Burrell, Seibert, and Robertson, will illustrate in a general way those formerly employed. The gas mixture to be analyzed was measured in a buret, transferred to a liquefying bulb surrounded by a cold bath, and a distillate pumped off and collected over mercury. This distillate was then transferred to a buret for measurement. The residue remaining was allowed to warm up and likewise pumped off and measured. Several distillations and combinations of the resulting fractions were necessary to obtain each of the components of the mixture in sufficient purity for accurate results, so that a determination of all the constituents was a long and complicated procedure.

## NEED OF AN IMPROVED METHOD

Gas distillation presented a wide field for extension in 1918, when the Bureau of Mines undertook the production of helium for the Army and Navy Aircraft Divisions.

At the experimental plant erected at Petrolia, Texas, and operating under the Jefferies-Norton system, the chemical laboratory was confronted with the necessity of preparing pure methane, ethane, and propane for vapor pressure measurements; and also with the problem of a systematic investigation of several types of gases peculiar to the liquefaction plant and containing appreciable percentages of the hydrocarbons of the series  $C_n H_{2n+2}$ , heavier than ethane.

The work was undertaken with the apparatus and method suggested by Burrell, Seibert, and Robertson.<sup>4</sup> It was found that an accurate separation of many of the particular mixtures examined required almost a week's time—i. e., 36 to 48 hours continuous operation. As a plant control method this distillation process was entirely out of the question. It held little value from the more deliberate standpoint of investigation and interpretation of plant operation, since affairs progressed so rapidly that week-old information possessed relatively small importance.

## DEVELOPMENT OF AN IMPROVED METHOD

An apparatus and method was therefore developed which was capable of accomplishing the same results as the previous method, but in a fraction of the time formerly required.

The apparatus constructed employs several improvements in the technic of gas manipulation, which have been in gen-

<sup>4</sup> *Bur. Mines, Tech. Paper 104* (1915).

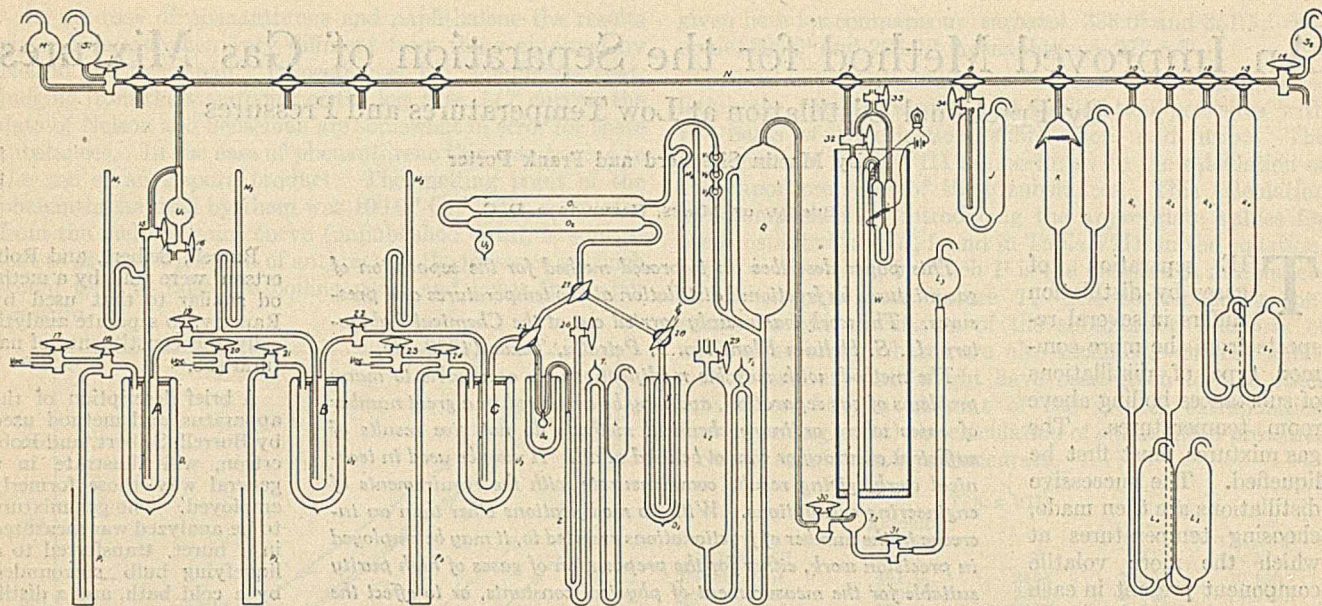


FIG. 1—APPARATUS FOR SEPARATION OF GAS MIXTURES BY FRACTIONAL DISTILLATION AT LOW TEMPERATURES AND PRESSURES

A, B, C = Distillation Bulbs

D<sub>1</sub>-D<sub>4</sub> = Dewar Tubes

H = Reservoir for Cleaning Solution

J = Adsorption Pipet

K = Combustion Pipet

L<sub>1</sub>-L<sub>7</sub> = Leveling Bulbs

M<sub>1</sub>-M<sub>4</sub> = Barometric Manometers

O<sub>1</sub>, O<sub>2</sub> = P<sub>2</sub>O<sub>5</sub> Tubes

P<sub>1</sub>-P<sub>3</sub> = Mercury Seal Pressure Regulators

Q = Töpler Pump

R<sub>1</sub>-R<sub>4</sub> = Gas Reservoirs

S<sub>1</sub>, S<sub>2</sub> = Mercury Reservoirs

T<sub>1</sub>-T<sub>3</sub> = Air Traps

U<sub>1</sub>, U<sub>2</sub> = Mercury Traps

V<sub>1</sub>-V<sub>3</sub> = Valves for Töpler Pump

W = Gas Measuring Buret

X = Liquefying Bulb for Vapor Pressure Manometer

Z = Vapor Pressure Manometer

(Cap.) Tee Cocks = 2-13

Y Cocks = 25-28

3-Way Cocks = 1, 14, 17, 18, 20, 21, 23, 24, 29, 32, 34

2-Way Cocks = 15, 16, 19, 22, 26, 30, 31, 33

Y = Bulb Filled with Activated Coconut Charcoal

N = Distributor Chain

eral use for some time and were suitable for adaption to this problem. It abandons the older ideas of separate pieces of apparatus, combining, as it does all the necessary steps of gas condensation, distillation, pumping, storage, volume measurement, and distribution into one complete unit, independent of auxiliary parts. The distribution of gas in a mercury-filled train eliminates all dead capillary space.<sup>5</sup> The system of multiple distillation bulbs permits the removal of vapors by rapid condensations, and eliminates the greater part of the work formerly assigned to the Töpler pump.

The details of the apparatus (Fig. 1) and the manner in which a separation is carried out are best described by taking as an example the fractionation of the natural gas from the Petrolia field. This gas has for its constituents helium, nitrogen, methane, ethane, propane, butane, and also small amounts of the higher saturated hydrocarbons. No attempt was made to separate the helium, nitrogen, and methane (this group being treated as a single fraction), since satisfactory temperatures for these distillations were not available, and other methods of analysis of this fraction were preferable from a practical standpoint.

To prepare the apparatus for an analysis, clean mercury is allowed to displace all gas from the distributor train N, Töpler pump head Q, buret W, and reservoirs R. An oil-immersed gear pump connected at Cock 28 quickly evacuates the distillation train, including the trap U, distillation bulbs A, B, and C, the manometer Z, with liquefying bulb X, and the P<sub>2</sub>O<sub>5</sub> tubes o, to a pressure of about 0.1 mm. Cock 28 is then turned to a tube Y, filled with activated coconut charcoal and surrounded with liquid air. Complete exhaustion of the distillation train is attained within 3 minutes, by adsorption of the residual air by the cold charcoal. The charcoal tube is then shut off from the train.

<sup>5</sup> Allen and Lyder, "Chemical Survey of Natural Gases of Kansas and Oklahoma," p. 39.

The three distillation bulbs are then cut off from one another by the interposing cocks, and surrounded with liquid air contained in closed Dewar tubes. A system of three-way cocks connects the Dewar tubes to the oil-immersed gear vacuum pump, the atmosphere, or a mercury pressure seal, P. By this arrangement the liquid air within the Dewar tubes may be made to boil at pressures ranging from less than 0.1 to 2 atmospheres, and a corresponding temperature range (depending of course on the age of the liquid air) of  $-180^{\circ}$  to  $-208^{\circ}$  C. is available.

The gas mixture to be examined is measured in the buret and then transferred through the distributor train into bulb A, where it partially liquefies at  $-190^{\circ}$  C. It is evident that the nitrogen and helium will not condense at this temperature and a pressure of less than atmospheric, and these two constituents, therefore, never properly enter the actual process of distillation, except to the small degree, due to their slight solubilities as uncondensed gases in the hydrocarbon liquid phase. Their separation may be regarded almost entirely as an actual separation by fractional condensation, a case that will occur very rarely. (It is unfortunate that a great many experimenters have used purely condensation processes under the name of distillation, when an accurate separation could only have been attained by an actual distillation.) It has been found in practice that all the helium and nitrogen, together with a small part of the methane, may be drawn off at once from A, at  $-190^{\circ}$  C., through B and C into the Töpler pump, which delivers directly into the buret for measurement. This fraction carries no ethane with it. A great saving in the time required for any one analysis is effected by this preliminary removal of uncondensed gases. The greater part of the methane now remains with the heavier hydrocarbon fraction in A. In order to accelerate its separation, the liquid air surrounding A is put under pressure, and a temperature of  $-180^{\circ}$  to  $-183^{\circ}$  C. is employed for the

next distillation. This raises the vapor pressure of the methane from approximately 4 cm. to between 6 and 10 cm., at the same time keeping the vapor pressure of the ethane well under 0.1 mm. The methane is then transferred from *A* to *B* by simply causing the liquid air in *B* to boil under reduced pressure (at a temperature of, say,  $-205^{\circ}\text{C}.$ ), which effectively removes methane vapor from *A* and condenses it in *B*. A second distillation from *B* to *C* is made by allowing *B* to warm up to the boiling point of liquid air at atmospheric pressure ( $-190^{\circ}\text{C}.$ ) and surrounding *C* with liquid air boiling under reduced pressure. Then by closing the cock between *C* and *B* and allowing *C* to warm up to room temperature, the pure methane fraction in *C* is vaporized and easily removed by the Töpler pump to the buret, where it is measured with the uncondensed  $\text{He} + \text{N}_2$  fraction. The residue of higher hydrocarbons, remaining in *A* and *B*, is now allowed to warm up to room temperature, completely vaporized, and is then recondensed at  $-183^{\circ}\text{C}.$  and fractionated as before, in order to free the residue from any traces of methane. This distillate is added to the  $\text{He} + \text{N}_2 + \text{CH}_4$  fraction already obtained. The vapor pressure of ethane always remains so low at these liquid air temperatures that practically none of it is removed with the last methane distillates. In practice, it was found unnecessary to provide for the possibility of ethane being present in the methane fraction, when ordinary analytical separation was desired.

The separation of ethane from the remaining higher hydrocarbons is effected in a similar way, except that the distillation temperature employed is between  $-145^{\circ}$  and  $-150^{\circ}\text{C}.$ , and the receiving temperature is that of liquid air. The vapor pressure ratio of ethane to propane at  $-150^{\circ}\text{C}.$  is approximately 4 to 0.4 mm. For the separation of propane from the butane plus heavier hydrocarbon fraction a temperature of  $-120^{\circ}\text{C}.$  was used, with a corresponding propane-butane vapor pressure ratio of 5 to 0.2 mm. The various steps for a complete fractionation of a sample of Petrolia gas are shown in Table I. The fractionating diagram here shown differs somewhat from the scheme described in the text, in that it provides for fractionation of possible traces of ethane from the  $\text{He}-\text{N}_2-\text{CH}_4$  fraction.

The fractions after measurement may be stored in reservoirs, *R*. The amount of methane in the methane-nitrogen fraction can be determined by combustion, using the combustion pipet *K*<sup>6</sup> and absorption pipet *J*,<sup>7</sup> which preferably are placed on opposite sides of the buret. If percentage helium is desired, it may be determined by the Cady<sup>8</sup> method.

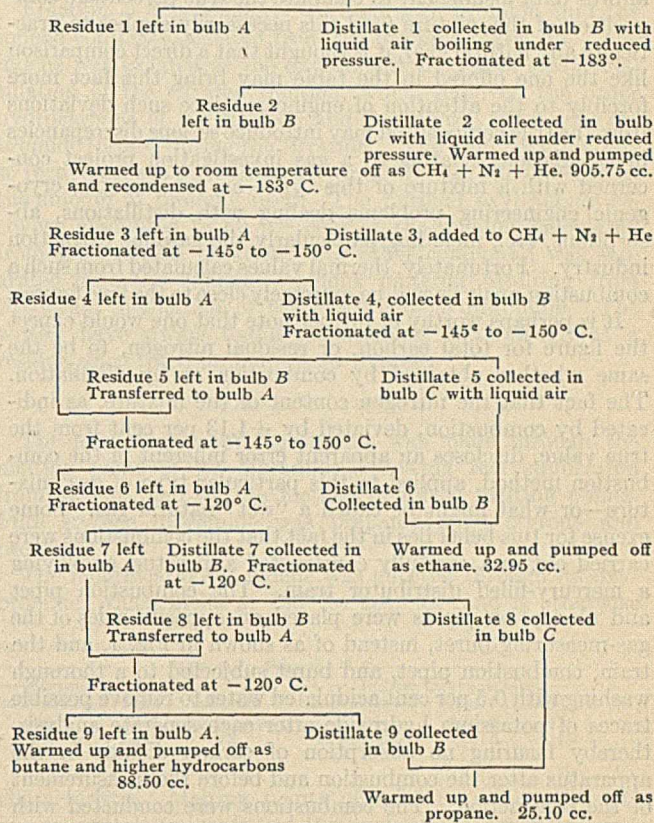
#### ACCURACY OF THE ANALYSIS

In practice, by following the fractionation chart of Table I, check analyses have agreed within the range 0.02 to 0.10 per cent. It is necessary to employ careful manipulation in order to obtain checks to the second decimal place. It also follows that precision volume measurements, an all-glass apparatus with no rubber connections, accurately ground, and suitably lubricated stopcocks are all necessary requirements. The portions of the apparatus confining gas over mercury must present no gas traps; and at all points where mercury enters the apparatus from air contact, air traps must be provided. An example of such an analysis is given in Table I.

A better test of the accuracy of analyses by fractional distillation of natural gas, according to the method charted in Table I, has recently been made by Frank Porter and F. W. Schroeder in the Cryogenic Research Laboratory, Washington, D. C. Pure methane, ethane, and propane were pre-

pared and tested as follows: Commercial nitrogen was freed from any impurities that would interfere by passing through a bulb surrounded with liquid air. A known mixture of these gases was made up similar in composition to the natural gas from the Petrolia field. This mixture was analyzed, using the regular procedure illustrated in Table I. For the sake of comparison, analysis of the same mixture was made by ordinary combustion with oxygen over a glowing platinum helix, the hydrocarbon fraction being calculated as methane and ethane from the contraction and carbon dioxide, and nitrogen taken by difference from 100. These results are summarized in Table II.

TABLE I—FRACTIONATION OF PETROLIA GAS BY IMPROVED SYSTEM  
Original Volume 1052.4 cc.  
Fractionated at  $-183^{\circ}\text{C}.$



GAS	VOLUME	
	Cc.	Per cent
Original volume of mixture.....	1052.4	100.00
$\text{CH}_4\text{N}_2\text{He}$ .....	905.7	86.06
$\text{C}_2\text{H}_6$ .....	32.95	3.13
$\text{C}_3\text{H}_8$ .....	25.10	2.39
$\text{C}_4-\text{H}_{10}$ + heavier $\text{C}_n\text{H}_{2n+2}$ .....	88.50	8.41
TOTAL.....	1052.2	99.99
Deviation from original volume ...	0.2	0.01

It will be seen that, with no more than three distillations for each component, the errors are of the approximate magnitude of 0.1 per cent. This error is about equal to the probable error in estimating volumes in the present instance. It is then clearly indicated that the accuracy easily falls within the limits required by all technical gas investigations. It is evident that the accuracy of the method is at the option of the operator. By increasing the number of fractionations for each component, the accuracy can be made to approach the limit imposed by even the most exact method available for measuring gas volumes.

The results of the analysis by the combustion method, however, deviate by approximately 5 per cent from the true values. This deviation should possibly not be considered entirely in the light of a true error, since the greater percentage

<sup>6</sup> Weaver and Ledig, THIS JOURNAL, 12, 368 (1920).

<sup>7</sup> Bur. Mines, Bull. 42, gives details of combustion analyses.

<sup>8</sup> Cady and McFarland, J. Am. Chem. Soc., 29, 1524 (1907).

TABLE II—ANALYSIS OF A KNOWN MIXTURE<sup>a</sup> OF PURE GASES BY FRACTIONAL DISTILLATION

COMPOSITION OF MIXTURE OF PURE GASES Gas	Cc.	OF PURE GASES Volume	ANALYSIS OF MIXTURE BY DISTILLATION—PER CENT			ANALYSIS OF MIXTURE BY COMBUSTION WITH OXYGEN OVER GLOWING PLATINUM HELIX				Per cent Deviation <sup>b</sup> from True Value	
			Composition	True Value	Deviation from True Value	(1)	(2)	Per cent Average	Per cent Average		
Nitrogen	136.80	28.67	88.87	88.99	+0.12	29.7	29.9	29.8	85.3	-3.7	{ +1.13 -4.7
Methane	287.25	60.20				55.4	55.6	55.5			
Ethane	27.85	5.84	11.13	{ 5.85 5.16	{ +0.01 -0.13	14.9	14.5	14.7	14.7	+3.6	{ +8.86 -5.29
Propane	25.25	5.29				14.9	14.5	14.7			
TOTAL	477.15	100.00	100.00	100.00	0.00	100.0	100.0	100.0	100.0		0.00

<sup>a</sup> Mixture approximates the composition of Petrolia natural gas.

<sup>b</sup> The composition was calculated as if methane and ethane were the only hydrocarbons present, and deviation from true value must necessarily follow.

of the difference necessarily follows from the computation on the basis of the presence of methane and ethane only, which was known to be untrue in the present case. While it is generally known to those familiar with the method that a combustion of a mixture of more than two hydrocarbons affords data insufficient to compute the true percentage composition of the mixture (and this necessarily applies to practically any natural gas), it is thought that a direct comparison like the one offered in the table may bring this fact more forcibly to the attention of engineers, since such deviations from the true composition may introduce serious discrepancies in calculations relating to a gas investigation project concerned with a mixture of this type—as, for example, cryogenic engineering problems dealing with distillations, absorptions, etc., including particularly the gasoline extraction industry. Fortunately, thermal values calculated from such a combustion analysis will be extremely close to the true figures.

It is perhaps worthy of further note that one would expect the figure for total carbon, or residual nitrogen, to be the same whether obtained by combustion or by distillation. The fact that the nitrogen content of the mixture, as indicated by combustion, deviated by +1.13 per cent from the true value, discloses an apparent error inherent in the combustion method, applied to this particular type of gas mixture—or what might be called a "wet" natural gas. Some excuse for this belief lies in the fact that the combustions were carried out in a carefully constructed apparatus, employing a mercury-filled distributor train. The combustion pipet and absorption pipets were placed on opposite sides of the gas-measuring buret, instead of as shown in Fig. 1, and the train, combustion pipet, and buret subjected to a thorough washing with 0.5 per cent acidulated water to remove possible traces of potassium hydroxide after each separate analysis, thereby insuring no absorption of carbon dioxide in the apparatus after the combustion and before the measurement of the contraction. The combustions were conducted with a measured excess of pure oxygen, and the wire temperature was carried as high as possible in order to effect as complete a combustion of methane and the heavier hydrocarbons as possible. After one to two hundred such combustions the black deposit collected from the dome of the combustion pipet revealed the distinct presence of carbon. It would seem doubtful if complete combustion is ordinarily attained over a glowing platinum helix with a "wet" natural gas. This point should, of course, be made the subject of further study.

#### PREPARATION OF PURE GASES

The preparation of very pure gases, suitable for the measurement of physical constants, is a difficult matter, since in the generation of any gas there is invariably introduced a number of impurities, which in many cases cannot be removed by chemical methods. Especially is this true in the case of organic compounds where the impurities are apt to be homologs of the gas prepared. Fractional distillation is often the logical procedure for final purification.

The procedure for obtaining gases in the pure state is the same as already described, except that the distillations are continued as many times as necessary by transferring the

residue left in *B* to *A*, and distillate left in *C* to *B*, and then redistilling from *B* to *C*, discarding the end fractions. A transfer from one bulb to another is made by allowing the one to come to room temperature, while open to the other surrounded with liquid air.

#### TEST OF PURITY

Vapor pressure measurements have been used as the test of purity, based on the fact that vapor pressure of a pure substance does not change as the ratio of the liquid volume to the gas volume is varied. This seems to be the best available method, and has been regularly employed by Travers, Onnes, and others.<sup>9</sup> The manometer Travers describes was made an integral part of the apparatus, connecting through a three-way cock (*Z*, Fig. 1) to bulb *C*.

In the manner described above, with the prescribed tests of purity accepted as a criterion, pure methane, ethane, and propane were prepared from Petrolia gas. The preparation was repeated in the case of methane, purification being made of a gas generated from methyl iodide in the presence of zinc-copper couple, and passed in succession through palladium asbestos at 100° C., and a condensation tube at -150° C., 760 mm. pressure, before submitting to distillation. The vapor pressure test in no case showed a variation of as much as one millimeter. Spectroscopic examination was used to supplement the vapor test and no nitrogen was detected by this means. The preparation of methane from natural gas by fractionation required about eight hours. The older methods demanded weeks of tedious manipulation to attain the same end.

<sup>9</sup> Travers, "Study of Gases," p. 228.

#### European Mining Industry

Remarkable progress has been achieved in the reconstruction of the French mining industry, according to George S. Rice, chief mining engineer of the Bureau of Mines, who has returned to this country after completing a study, occupying several months, of conditions in the mining industries of France, Great Britain, Belgium, Poland, and Czechoslovakia. Underground, the French mines have recovered to such an extent that they are producing about 70 per cent of the normal coal output. When all the water has been pumped out of the mines, the coal production of Northern France will be greatly increased over that of the pre-war period.

Novel methods for obtaining petroleum, involving the mining of oil sands and their subsequent treatment at the surface, are employed in Alsace and near Hanover. This makes possible a greater recovery of the petroleum, two-thirds of which is left in the ground after ordinary extraction by wells.

In Great Britain and France the employment of rock dust as a screen or barrier for the limitation of coal dust explosions to the immediate area of the explosion has been made compulsory. In France powdered coal has been widely adopted as a fuel. In Germany, near Hanover, novel methods are employed in the distillation of brown coal, a lignite quite different from American lignites, from which various oils, paraffin, and gas are being obtained. At Whitehaven, England, coal is being mined under the sea at a point four and one-half miles from the shore line.

As a result of Mr. Rice's visit to England the British government has already proposed that a joint program of research, covering various mining problems, be adopted. This program would include the exchange of technical information, of materials under test, of scientific apparatus, and possibly of research personnel. This proposal has been accepted by Secretary Work.

# Indene and Styrene—Constituents of Carbureted Water-Gas Tar<sup>1</sup>

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THE list of constituents which have been identified and may normally be expected to be present in coal tar is a long one. The compounds comprising this list have been discussed in the authoritative work of Lunge,<sup>2</sup> in which the literature had been well reviewed. In the case of carbureted water-gas tar but little work has apparently been done towards the identification of constituents. In a recent publication, Bateman,<sup>3</sup> in speaking of water-gas tar, states that "benzol, toluol, xylol, naphthalene, phenanthrene, and methyl anthracene have been identified." Downs and Dean<sup>4</sup> reported the identification of thiophene, benzene, toluene, *o*-, *m*-, and *p*-xylenes, mesitylene, naphthalene, and anthracene. In 1893, Deunstedt and Ahrens<sup>5</sup> reported an examination of condensate from the illuminating gas of the City of Hamburg, in which they found about 1 per cent of styrene and an unstated quantity of indene, but from their original paper the amount is judged to be only a few per cent. In a previous paper<sup>6</sup> it was pointed out that the natural condensate, "drip-oil," taken from the distributing systems of carbureted water-gas plants in the United States contained these two hydrocarbons—namely, indene and styrene—in amounts totaling 40 to 50 per cent of the condensate. It follows as a corollary that these two hydrocarbons should be found in water-gas tar. It is the belief of the writers that the most intelligent and profitable utilization of this by-product of the "gross" industry of gas manufacture is possible when it is based upon the fundamental information of molecular composition of the tar, and the physical and chemical

from the bromine used. The styrene dibromide so formed and recovered by the evaporation of the hydrocarbons other than styrene was found to be practically pure, and amounted to over 95 per cent of the amount calculated from the titration.

Fraction 3 was similarly titrated with bromine, and the indene content calculated from the bromine taken up. The indene was isolated as the oxybromide by gentle steam distillation of the titrated fraction, which removed the other hydrocarbons of the fraction and hydrolyzed the indene dibromide formed during the titration. The crude oxybromide so recovered was approximately equal to that calculated from the amount of bromine used. The purified oxybromide recovery amounted to 60 per cent of the amount calculated from the bromine titration. No other compound was separated from the residual resinous material resulting from the steam distillation of the crude indene dibromide. The writers have always found this resinous material left as a residue when the dibromide is so treated.

## IDENTIFICATION

The identification of the styrene was made through the melting point of its dibromide following recrystallization from alcohol, and by the method of mixed melting points. Pure styrene dibromide was prepared from styrene and bromine.

The identification of indene was effected through its oxybromide, which melts at 130° to 131° C. and is otherwise

Sample	DETERMINATION OF STYRENE AND INDENE						MELTING POINTS—° C.					
	Oils Boiling below 190° C.	PERCENTAGE OF TAR SAMPLE			Styrene	Indene	Styrene Dibromide					
		Fractions					From Fraction 2	Pure	Mixture	Indene Oxybromide		
A	5.3	1.0	1.4	2.9	0.7	1.9	72.5	73.5	72.5 to 73	130	130.5	130
B	5.5	1.5	2.1	1.9	0.9	1.2	73	73.5	73	129 to 130	130.5	130

properties of the constituents. With this point of view, and in the interests of the dissemination of knowledge, the writers have isolated, identified, and measured the indene and styrene in two typical samples of water-gas tar. The experimental data in their essentials are given below.

## ISOLATION AND DETERMINATION

The method employed in removing the oils boiling below 200° C. was to pass steam through 1000-cc. samples of the tar maintained at 150° C. The oil thus separated was distilled over a 14-inch bead column and collected in three fractions—namely, (1) boiling up to 130° C., (2) boiling between 130° and 160° C., and (3) boiling 160° to 190° C.

Fraction 2 was titrated with bromine (in carbon tetrachloride solution), and the styrene content was calculated

characteristic. Melting points of mixtures of equal parts of the crystals isolated and the oxybromide derivative prepared from indene were taken, and are reported below.

Sample A was a water-gas tar of specific gravity (20° C.) 1.058 and low naphthalene, free carbon, and water content. It was taken from tar storage, and was typical for the plant.

Sample B was a water-gas tar of specific gravity (20° C.) of 1.176, and contained in comparison with Sample A much naphthalene, free carbon, and water. It was taken from the works separator of the plant in which it was produced.

In the table which follows is given the experimental data pertinent to the purpose of the paper. The percentages are all based on 1000-cc. of tar as sampled, and are in terms of volume throughout. The temperatures are corrected values.

<sup>1</sup> Received June 8, 1923. Published by permission of the Director, U. S. Bureau of Mines.

<sup>2</sup> "Coal Tar and Ammonia," 5th ed., 1916.

<sup>3</sup> U. S. Dept. Agr., Bull. 1036, 73.

<sup>4</sup> THIS JOURNAL, 6, 366 (1914).

<sup>5</sup> "Jahrbuch der Hamburgerschen wissenschaftlichen Anstalten," 1893, p. 132.

<sup>6</sup> Brown, Chairman of Committee on Deposits in Gas Pipes and Meters; "Deposits in Gas Pipes and Meters," American Gas Association, Proceedings Technical Section, 1922.

The Department of Commerce has announced that after January 1, 1924, "too many asphalt grades" no longer will be the complaint, and that on the date mentioned the recommendations adopted at its recent asphalt paving conference will become effective and the number of asphalt grades for use in the construction of sheet asphalt, asphaltic concrete, asphalt macadam, and surface-treated pavements will be reduced from eighty-eight to nine. The number of asphalt grades used as joint filler in the construction of brick and block pavements and various other types has been reduced from fourteen to four.

# The Influence of Hydrogen-Ion Concentration in the Fixation of Vegetable Tannins by Hide Substance<sup>1,2</sup>

By Arthur W. Thomas and Margaret W. Kelly

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EVER since 1899, when Hardy<sup>1,\*</sup> first defined the isoelectric point, the importance of considering hydrogen-ion concentration when dealing with protein solutions has come increasingly to notice. Procter and Wilson<sup>2</sup> in 1916 explained the changes in swelling of gelatin jellies in acid solutions of different strengths, with and without added salt, by the theory of membrane equilibria which had been published by Donnan<sup>3</sup> in 1911. During the past few years Loeb<sup>4</sup> has made a very complete study of the effect of change in hydrogen-ion concentration and added salt on the physical properties of protein solutions, giving an adequate explanation by means of the Donnan theory for changes in electrical potential difference, viscosity, swelling, and osmotic pressure with change in pH of solution and concentration and kind of added salt.

Since hydrogen-ion concentration has been shown to have such an important bearing on the properties of protein solutions, it was therefore decided to study the effect of changes in hydrogen-ion concentration on the rate of tanning of collagen with various vegetable tan liquors, hoping thereby to throw some light on the nature of this complex reaction.

## MATERIALS

In all experiments American standard hide powder was used as the source of hide protein. This was first sifted to remove 100-mesh particles in order to avoid the loss of material fine enough to pass through the filter cloth used in washing, then thoroughly extracted with chloroform to remove fat, and air-dried. The moisture in this stock sample was determined by heating at 100° C. in a vacuum oven for 5 hours, and all weights of hide powder are reported on this moisture-free basis.

As sources of tannin, six different tanning extracts, quebracho, gambier, hemlock bark, oak bark, larch bark, and wattle bark, were employed. A concentrated stock solution of each was prepared by dissolving in water at 85° C. After cooling, insolubles were removed by centrifuging and filtering. Total solids in this clear, concentrated extract were determined by the American Leather Chemists Association method,<sup>5</sup> and all concentrations are reported on the basis of this determination.

## METHOD

The method employed for determination of tannin fixed by the hide powder is essentially that proposed by Wilson and Kern<sup>6</sup> in their modified method, adopting the practical definition of tannin as that material, present in certain

<sup>1</sup> Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

<sup>2</sup> Contribution No. 422 from the Chemical Laboratories, Columbia University. Taken from a part of the dissertation submitted by Miss Kelly in partial fulfillment of the requirements for the degree of philosophy, Faculty of Pure Science, Columbia University, 1923.

\* Numbers in text refer to bibliography at end of article.

*The rate of combination of hide protein with vegetable tannins is a marked function of the hydrogen-ion concentration and of the concentration of the vegetable tannin solution. The results obtained are readily understood in the light of the modern knowledge of the physical chemistry of the proteins and of vegetable tanning extracts. Explanations for changes in behavior with respect to these factors have been offered, based mainly upon the Donnan theory of membrane equilibria, the Procter-Wilson work upon swelling of colloid jellies, the Procter-Wilson theory of vegetable tanning, and the work of Loeb upon proteins.*

vegetable extracts, which is capable of precipitating gelatin from solution, and of forming, with hide protein, a compound that is resistant to washing with water. The Wilson and Kern determination involves simply the measurement of increase in weight of a sample of hide powder, after tanning and thorough washing. For estimation of tannin in an extract by their method, the weight of hide powder and concentration of extract are so chosen as to insure, in 6 hours' contact, complete removal of tannin from the extract as evidenced by a negative gelatin-salt test on the filtrate. Since in the work here recorded it was desired, however, to obtain a comparative measure of the amount of tannin fixed under varying conditions, it was of course necessary to arrange conditions so as to have an excess of tannin in the filtrate in all cases.

In all experiments 2,000-gram samples (dry basis) of the specially purified hide powder were placed in 400-cc. rubber-stoppered bottles. To these were added 100-cc. portions of the tanning extract, and the bottles were rotated for the desired length of time at room temperature in a tumbling machine. The tanned hide powders were then filtered off in Wilson and Kern extractors, using a fine grade of cambric as filter cloth. Samples of the filtrates were saved for later tests, and the hide powders were washed with distilled water until the washings gave a negative test with ferric chloride, thereby indicating the complete removal of tannins and non-tans. The tanned portions of hide powder were air-dried in the extractors and transferred to weighing bottles. The samples were given a preliminary drying for 5 hours at 70° C. in an atmospheric oven, and finally were heated at 100° C. in a vacuum oven for 5 hours. The increase in weight (dry basis) over the original 2,000 grams of anhydrous hide powder represents the amount of tannin fixed.

Filtrates were tested for tannin in every case by the gelatin-salt reagent under the conditions established by Thomas and Frieden,<sup>7</sup> where delicacy may be claimed of at least 1 part of tannin in 100,000 parts of solution. The older methods for estimation of the tannin content of an extract, by measurement of the change in concentration of the tanning liquor before and after shaking with hide powder, are subject to large errors due to the well-established fact that hide powder removes certain non-tans as well as tannins from tanning solutions, and also to the fact that they fail to take account of changes in concentration due to absorption of water by hide powder from the extract. In the Wilson-Kern method these errors are eliminated, as the adsorbed non-tans are removed in the washing of the tanned hide powder. Moreover, as pointed out by Thompson, Seshachalam, and Hassan,<sup>8</sup> the tanning content of an extract, as determined by the older methods, varies with the acidity of the tanning solution. Wilson and Kern,<sup>9</sup> on the other hand, have shown that their method gives a practically constant tannin value for an extract over a pH range from 3.6 to 7.3.

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## DETERMINATION OF PROPER CONCENTRATION

Since it would be necessary in the determination of the influence of hydrogen-ion concentration upon tannin fixation in all cases to be certain of insuring an excess of tannin, in order to have a true measure of the relative amounts of tannin fixed under varying conditions, it was necessary first to establish at what concentration the filtrates would give a positive gelatin-salt test by a study of the concentration curve for each extract for a 24-hour tanning period. The method outlined above was used. The results are summarized in Table I and Fig. 1.

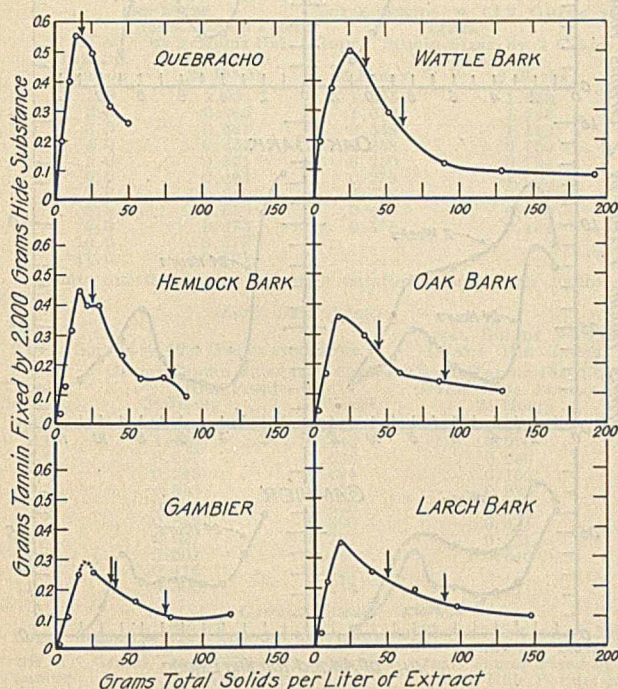


FIG. 1

The arrows in Fig. 1 indicate the concentrations adopted for study of the influence of hydrogen-ion concentration reported later in this paper.

Observation of the curves indicates that all the extracts show a characteristic rise to a maximum, followed by a sharp drop, as the concentration of the extract increases. The maximum point in each case occurs at a concentration of the extract equal to 15 to 25 grams total solids per liter, and is always in the neighborhood of the point at which the first positive gelatin-salt test was obtained on the filtrate.

These results agree very well with those obtained from a similar study of the concentration factor which has been reported from this laboratory.<sup>10</sup> Similar types of concentration curves have been noted by Moeller<sup>11</sup> and by von Schroeder and Paessler<sup>12</sup> for the adsorption of tannic acid by hide substance, who, however, used the older methods for estimation of tannin—i. e., by analysis of an aliquot of the equilibrium solution. Most investigators have confined themselves, however, to a study of adsorption from dilute solution, and as a consequence have reported curves of the usual parabolic form expected for typical adsorption, which, in more extended concentration, experiments show to be erroneous.

The explanation of this typical concentration curve, characterized by a rise to a maximum, followed by a sharp decline, cannot be ascribed to variations of hydrogen-ion concentration of the extract with dilution. The pH of the extracts, measured electrometrically, showed a very slight but regular increase in acidity upon dilution, but the change

was too slight to be of any significance here. The explanation must be sought elsewhere. Three different factors are involved:

1—The surface of the hide powder particles, at a concentration of 15 to 20 grams total solids per liter, becomes so heavily tanned that the particles are rendered impermeable to the tanning solution. Consequently, the interior of the particles is relatively unaffected, resulting in a smaller amount of tannin being fixed from the more concentrated solutions. This assumption was offered in 1898 by von Schroeder and Paessler to explain a similar concentration curve obtained by them for the adsorption of tannic acid by hide.

2—A second factor, probably operating to decrease the amount of tannin fixed in a given period of time from the more concentrated solutions, is that, with increasing concentration, an increased aggregation of the tannin particles would be expected, thereby causing a lowered rate of diffusion into the hide substance. Since diffusion into the hide particles must precede fixation, less tannin would be fixed in a given time as a result of this increase in aggregation of particles.

3—Finally, Thomas and Foster<sup>13</sup> have shown for quebracho that the electrical potential difference of the tannin particles against the aqueous phase decreases with increase in concentration of the tanning solution. Probably this latter factor is the more important one in retardation of tanning upon increase of concentration of the extract, since, as will be shown later, anything which effects a reduction of the potential difference at the surface of the tannin particles will cause a decrease in the rate of tanning. Moreover, concomitant with increasing concentration of the extract there is a higher concentration of non-tans. And since these non-tans diffuse much more rapidly into the hide substance than do the tannins, owing to their lower molecular weight, their effect would tend to counteract the retardation due to heavy surface tannage and aggregation of the tannin particles.

## EFFECT OF CHANGE OF pH OF THE TANNING SOLUTION

Having determined a suitable concentration for use in the pH series of experiments, by the preliminary study of the concentration factor, as described above, 100-cc. portions of the extract to be studied were prepared in which the pH values varied from 1.0 to 11.0. The adjustment to the desired concentration of hydrogen ion was made by addition to the given amount of stock solution, before dilution to 100 cc., the required amount of 0.5 M hydrochloric acid or 0.5 M sodium hydroxide, previously determined by electrometric titration of a sample of the extract. Considerable difficulty was experienced in the titration of the tan liquors in the pH range from 6.0 to 8.0, due probably to reduction potentials.

TABLE I—EFFECT OF CONCENTRATION UPON FIXATION OF TANNIN

Grams Total Solids per Liter Extract	Grams Tannin Fixed by 2 Grams Hide Powder	Reaction of Filtrate with Gelatin-Salt Reagent	Grams Total Solids per Liter Extract	Grams Tannin Fixed by 2 Grams Hide Powder	Reaction of Filtrate with Gelatin-Salt Reagent
Quebracho (pH = 4.6)					
5.01	0.196	—	5.12	0.197	—
10.03	0.400	Very slightly +	12.8	0.378	—
15.04	0.546	+	25.6	0.498	+
25.07	0.482	+	51.2	0.289	+
37.6	0.316	+	89.6	0.121	+
50.1	0.263	+	128.0	0.094	+
			192.0	0.084	+
Hemlock (pH = adjusted to 5.0)					
3.36	0.036	—	3.95	0.045	—
6.64	0.136	—	9.87	0.226	—
11.15	0.315	—	19.74	0.353	slightly +
16.00	0.448	+	39.48	0.259	+
21.81	0.388	+	69.09	0.185	+
29.75	0.385	+	98.70	0.134	+
46.06	0.230	+	148.1	0.103	+
58.57	0.157	+			
73.94	0.167	+			
88.72	0.089	+			
Oak (pH = 4.0)					
3.38	0.045	—	3.13	0.015	—
8.45	0.171	—	7.83	0.107	—
16.90	0.363	—	15.7	0.253	+
33.80	0.300	+	31.4	0.262	+
59.21	0.187	+	54.8	0.162	+
84.50	0.131	+	78.5	0.103	+
126.8	0.114	+	117.7	0.119	+
Gambier (pH = 4.7)					

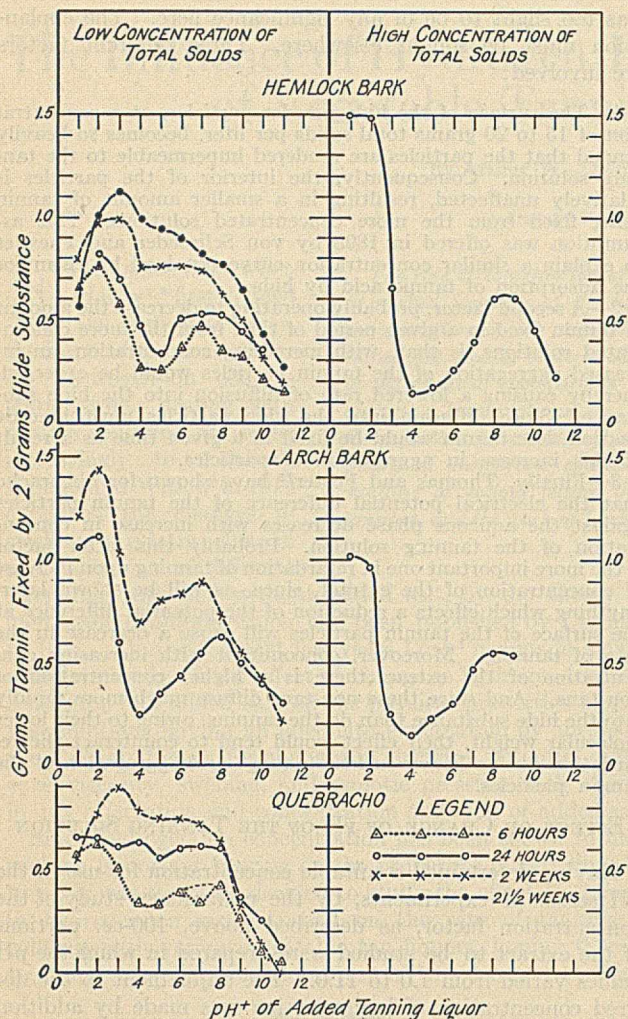


FIG. 2

Attempts were made in the earlier experiments to measure the pH of the tanning solution in equilibrium with the tanned hide powder at the end of the tanning period, since this value, of course, is the one of real significance in the Donnan effect. The measurements were attended with such great difficulty, due to electrode effects, that the results obtained were exceedingly unreliable, and in the range of pH from 6.0 to 8.0, were absolutely impossible to measure. Oxidation during the "drumming," especially in the alkaline range, probably results in the establishment of a reduction potential when measurements of the pH of the equilibrium solution by means of the hydrogen electrode are attempted.

TABLE II—CHANGE IN pH OF HEMLOCK BARK EXTRACT, 24-HOUR TANNING PERIOD

		A—Untreated Extract							
		2.0	3.0	4.0	5.0	6.0	7.0	8.0	
Original solution		2.0	3.0	4.0	5.0	6.0	7.0	8.0	
Equilibrium solution		2.2	3.2	4.0	4.7	(impossible to measure)			
		B—Clarified Extract							
		2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0 10.0
Original solution		2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0 10.0
Equilibrium solution		2.9	3.8	4.3	4.9	(impossible to measure)			

The use of buffer solutions was precluded since, as will be shown later herein and in a separate paper, the presence of salts influences the fixation of tannin to a remarkable degree. It should be noted that tanning solutions themselves show considerable buffer action in the acid range, due to the tannic acids present. Since it is believed that the Donnan effect is only responsible for the initial rate of tanning, while, from the practical point of view, the question of pH of the original solution is the most important one, the attempt to measure equilibrium pH values was abandoned.

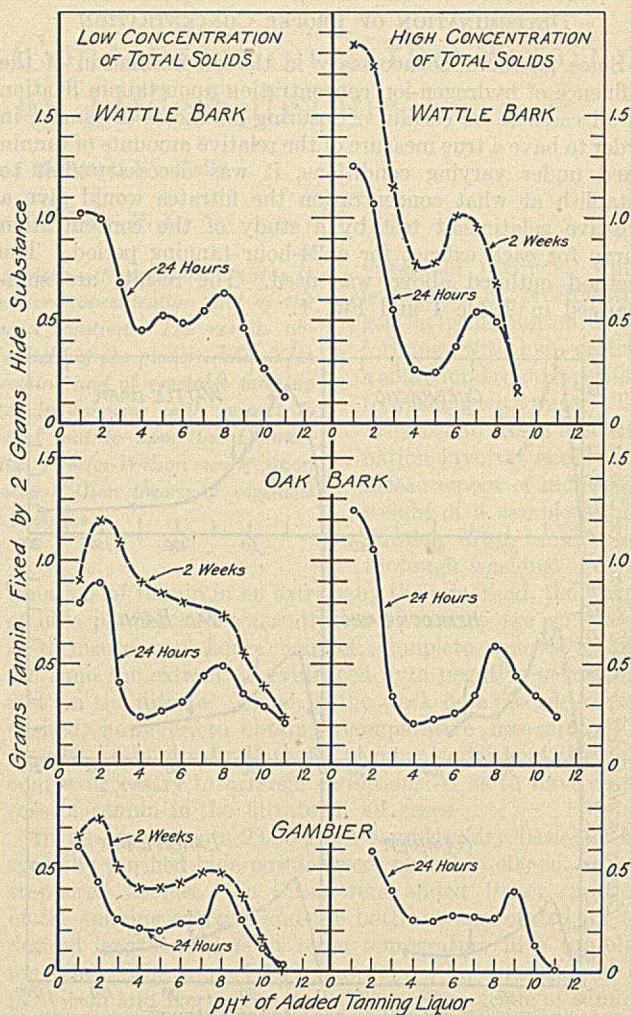


FIG. 3

The study was extended to include the fixation of tannin at different concentrations of hydrogen ion from each of the six extracts by the method previously described, at two different concentrations of each extract, except quebracho, and for different time intervals, as shown in Table III and Figs. 2 and 3.

TABLE III—EFFECT OF CHANGE IN pH OF TANNING SOLUTION UPON FIXATION OF TANNIN  
Hemlock Bark Extract

pH of Tanning Solution	TOTAL SOLIDS = 24.0 GRAMS PER LITER			TOTAL SOLIDS = 70.6 GRAMS PER LITER	
	6 Hours	24 Hours	2 Weeks	24 Hours	2 Weeks
1.0	0.653	...	0.687	0.557	1.494
2.0	0.756	0.812	0.889	1.020	1.478
3.0	0.570	0.686	0.921	1.119	0.657
4.0	0.273	0.466	0.694	0.995	0.134
5.0	0.261	0.330	0.703	0.940	0.174
6.0	0.367	0.495	0.698	0.894	0.265
7.0	0.478	0.520	0.675	0.825	0.385
8.0	0.353	0.519	0.670	0.767	0.605
9.0	0.318	0.438	0.438	0.635	0.601
10.0	0.215	0.346	0.249	0.419	0.449
11.0	0.155	...	0.119	0.269	0.223

Oak Bark Extract

pH of Tanning Solution	TOTAL SOLIDS = 42.3 GRAMS PER LITER		TOTAL SOLIDS = 88.2 GRAMS PER LITER
	24 Hours	2 Weeks	24 Hours
1.0	0.796	0.901	1.248
2.0	0.891	1.187	1.056
3.0	0.411	1.088	0.343
4.0	0.242	0.888	0.208
5.0	0.267	0.840	0.229
6.0	0.306	0.796	0.255
7.0	0.439	0.725	0.349
8.0	0.477	0.548	0.599
9.0	0.359	0.385	0.442
10.0	0.284	0.337	0.346
11.0	0.210	0.236	0.237

TABLE III—(Concluded)  
Quebracho Extract  
TOTAL SOLIDS = 18.3 GRAMS PER LITER

pH of Tanning Solution	Grams Tannin Fixed by 2 Grams Hide Powder in		
	6 Hours	24 Hours	2 Weeks
1.0	0.568	0.665	0.564
2.0	0.622	0.644	0.770
3.0	0.498	0.612	0.888
4.0	0.344	0.631	0.777
5.0	0.332	0.553	0.743
6.0	0.380	0.596	0.744
7.0	0.333	0.613	0.715
8.0	0.417	0.599	0.625
9.0	0.269	0.366	0.316
10.0	0.100	0.258	0.140
11.0	0.050	0.120	(-0.025)

## Wattle Bark Extract

pH of Tanning Solution	TOTAL SOLIDS = 36.9 GRAMS PER LITER		TOTAL SOLIDS = 61.4 GRAMS PER LITER	
	Grams Tannin Fixed by 2 Grams Hide Powder in	24 Hours	Grams Tannin Fixed by 2 Grams Hide Powder in	2 Weeks
1.0	1.034	1.255	1.840	
2.0	0.995	1.073	1.743	
3.0	0.681	0.548	1.152	
4.0	0.451	0.258	0.769	
5.0	0.521	0.250	0.784	
6.0	0.481	0.376	1.006	
7.0	0.549	0.538	0.957	
8.0	0.630	0.476	0.680	
9.0	0.473	0.175	0.151	
10.0	0.272	...	...	
11.0	0.131	...	...	

<sup>a</sup> Points omitted due to uncertain titration values with hydrogen electrode.

## Larch Bark Extract

pH of Tanning Solution	TOTAL SOLIDS = 49.4 GRAMS PER LITER		TOTAL SOLIDS = 98.8 GRAMS PER LITER	
	Grams Tannin Fixed by 2 Grams Hide Powder in	24 Hours	Grams Tannin Fixed by 2 Grams Hide Powder in	24 Hours
1.0	1.067	1.212	1.014	
2.0	1.111	1.443	0.970	
3.0	0.597	1.038	0.250	
4.0	0.248	0.694	0.150	
5.0	0.355	0.798	0.229	
6.0	0.441	0.825	0.303	
7.0	0.548	0.890	0.475	
8.0	0.627	0.727	0.551	
9.0	0.501	0.554	0.540	
10.0	0.416	0.421	...	
11.0	0.303	0.214	...	

## Gambier Extract

pH of Tanning Solution	TOTAL SOLIDS = *39.7) GRAMS PER LITER		TOTAL SOLIDS = 76.5 GRAMS PER LITER	
	Grams Tannin Fixed by 2 Grams Hide Powder in	24 Hours	Grams Tannin Fixed by 2 Grams Hide Powder in	24 Hours
1.0	0.796	0.657	...	
2.0	0.891	0.744	0.586	
3.0	0.411	0.510	0.393	
4.0	0.242	0.408	0.258	
5.0	0.267	0.412	0.249	
6.0	0.306	0.427	0.275	
7.0	0.439	0.476	0.272	
8.0	0.477	0.477	0.266	
9.0	0.359	0.368	0.391	
10.0	0.284	0.155	0.125	
11.0	0.210	(-0.011)	0.006	

An examination of the curves shows certain characteristics with change in pH of the tanning solution:

1—A minimum is always obtained in the neighborhood of pH of 5.0.

2—The curves rise from this minimum at 5.0 to a maximum at pH of 2.0 to 3.0 on the acid side, and to a maximum at pH of 7.0 to 8.0 on the alkaline side of this minimum, beyond which there is a drop in each case. In the concentrated solutions in the more acid range, the mass effect of the increased concentration of tannin is manifested by an increased fixation of tannin.

3—With high concentrations of the extract, the minimum at pH of 5.0 is even more marked than with the more dilute solutions, as would be expected from the results shown in the concentration curves, and there is usually a considerably greater amount of tannin fixed at corresponding pH values during identical time periods.

It will be recalled that the isoelectric point of collagen (hide powder, to be exact) has been established as at pH of 5 by work in this laboratory<sup>14</sup> using the dye fixation method, and by Porter<sup>15</sup> in England using degree of swelling. The work of Porter, who studied the swelling of hide powder over a pH range from -0.3 to 13.9, showed a minimum at pH of 4.8, while maxima appeared at pH of 2.2 and pH of 12.5. Wilson and Gallun,<sup>16</sup> in a study of the plumping of calfskin at 7° C. as a function of concentration of hydrogen ion,

observed two minimum points of plumping at pH of 5.1 and 7.6, respectively, and they suggest that these two points of minimum represent the isoelectric points of two different forms of collagen, which undergoes a change of form, possibly an internal rearrangement, in passing from acid to alkaline solution. Wilson and Kern<sup>17</sup> also observed a similar unexpected phenomenon for the swelling of gelatin at 7° C., one minimum at the generally accepted isoelectric point, pH of 4.7, and another at pH of 7.7. It is further to be noted that Thomas and Foster<sup>18</sup> have shown that vegetable tannin particles are amphoteric in character, with isoelectric points from 2.0 to 2.5, being negatively charged when the hydrogen-ion concentration falls below this figure and positively charged in more acid solutions. All these factors are involved in an explanation of the curves obtained.

## MECHANISM OF TANNING

Various theories have been put forward from time to time to explain the mechanism of tanning. Seguin (1796)<sup>19</sup> recognized that tanbark contained a "particular principle" which was soluble in water and gave a precipitate with gelatin, and he pointed out that this principle fixed itself upon the hide in tannage, effecting a "specific combination" between the tanning material and the hide. Knapp (1858)<sup>20</sup> considered tanning to result from a precipitation of the tanning material upon the fibers of the hide, resulting in a protective coating. This theory has been generally discarded, although Moeller<sup>11</sup> has recently revived the idea. The present-day theories are of two main types—one viewpoint being that tanning is a purely physical adsorption following the Freundlich adsorption isotherm, the other regarding tanning as of a chemical nature. Two important chemical theories have been advanced, one based upon the modern conceptions concerning the physical chemistry of the proteins, the other involving oxidation reactions of complex organic compounds.

PHYSICAL-CHEMICAL THEORY—This viewpoint rests upon the conception that proteins are amphoteric electrolytes capable of reacting to form salts with either acids or bases, according to the hydrogen-ion concentration of the solution in which the protein is placed, the isoelectric point being that point between these two regions at which ionization values of the protein, as base and acid, are equal and at a minimum. Starting with this viewpoint and employing the Donnan theory of membrane equilibria,<sup>3</sup> Procter<sup>21</sup> in 1914 and Procter and Wilson<sup>2</sup> in 1916 were able to explain quantitatively the swelling of gelatin jellies in acid solution, while in 1918,<sup>22</sup> by a more general treatment, the theory was extended to include the explanation of swelling of any colloidal jelly. Loeb,<sup>4</sup> working with gelatin, casein, and egg albumin, has extended the work to explain the other properties characteristic of colloidal behavior—viz., electrical potential difference, viscosity, osmotic pressure, and stability. All these properties are a function of the hydrogen-ion concentration of the protein solution and of the valency of the ion in combination with the protein. The curves, in which the values for any of the above-mentioned properties are plotted against the pH values of the equilibrium solution, exhibit points of minima at the pH corresponding to the isoelectric point of the protein, rising rapidly to maxima on either side as the pH of the solution moves away from the isoelectric point, and again falling off as the distance from the isoelectric point is further increased. For all monovalent ions in combination with the protein, maximum values for any given property are identical, while for all divalent ions a lower maximum value is obtained, but at the same pH value for the equilibrium solution. Moreover, added neutral salt always effects a reduction in value of the property in question—e. g., swelling, potential difference, etc.—while increase in

the amount of protein causes an increase in value of the property under consideration, providing that the concentration of hydrogen ion of the protein solution remains unchanged. The addition of nonelectrolytes is without effect on the value of the given property. The Donnan theory furnishes a complete and satisfactory explanation of this behavior, as

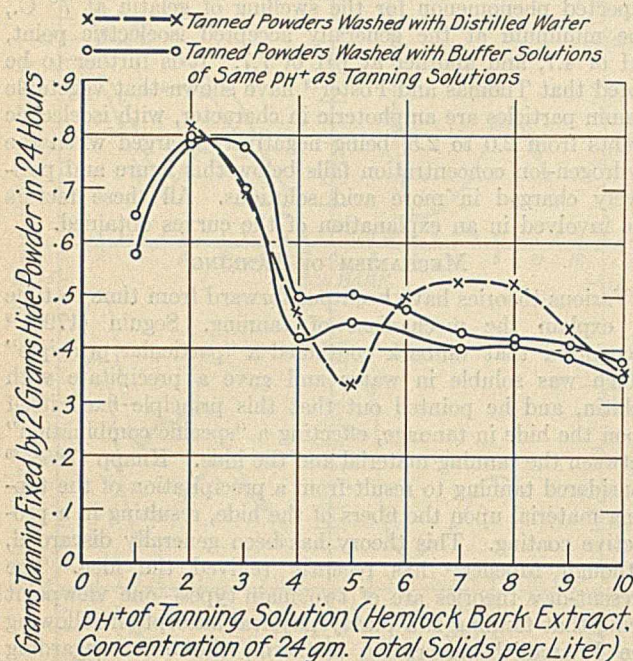


FIG. 4

has been shown by Procter and Wilson and by Loeb. This theory, based upon thermodynamic reasoning, predicts the equilibrium conditions which will arise in a system in which a membrane separates two solutions of electrolytes, one of which contains one ion which cannot diffuse through the membrane, while all other ions are readily diffusible. The result is an unequal distribution of the diffusible ions on the opposite sides of the membrane, such that, at equilibrium, the products of the concentrations of each pair of oppositely charged diffusible ions are the same for opposite sides of the membrane. As a necessary result of this unequal distribution of ions at equilibrium, there is developed an electrical potential difference which should have a minimum value at the hydrogen-ion concentration corresponding to the isoelectric point of the protein, and should exhibit maximum values, followed by a decline as the hydrogen-ion concentration of the solution is either increased or decreased from the isoelectric point. Moreover, this excess concentration of diffusible ions gives rise to osmotic pressure and, if we are dealing with a jelly, causes swelling.

The Procter-Wilson<sup>23,24</sup> theory of tanning is based upon this physico-chemical point of view. Collagen, when placed in a slightly acid solution, such as is commonly employed in tanning operations, is prevented from diffusing by its jelly-like character. Consequently, a Donnan equilibrium is set up which results in the establishment of a potential difference between the positively charged collagen and the solution. If all other factors are kept constant, the magnitude of this potential difference will depend upon the acidity of the solution. Likewise, each tannin particle is negatively charged. There is of necessity a resulting tendency of these opposite charges to neutralize each other, which is measured by the sum of their absolute values. It is this potential difference which is believed to provide the mechanism that brings the tannin particles into intimate contact with the collagen, and is therefore the most important factor in the control of the initial rate of tanning.

OXIDATION REACTIONS—A second chemical viewpoint is that tanning is the result of oxidation between quinone-like bodies present in the tanning solution and amino groups in the collagen molecule. The chief exponents of these oxidation theories, which are as yet very imperfectly understood for vegetable tanning, have been Meunier,<sup>25</sup> Fahrion,<sup>26</sup> and Powarnin.<sup>27</sup>

With this in mind, the rise in the curves in the acid range from the minimum at pH = 5.0 to the maximum at about pH = 2.0 is readily understandable from the viewpoint of the Procter-Wilson theory. The curves parallel the swelling curves of Porter<sup>15</sup> for collagen, and Loeb's work<sup>4</sup> with gelatin has demonstrated that changes in swelling and potential difference are practically coincident, each showing a minimum at the isoelectric point of the protein and maxima at identical pH values on either side of the isoelectric point. We should therefore expect collagen to be positively charged in this range of pH values, with a minimum potential difference at pH = 5.0, and a gradual increase in potential difference as the pH decreases to 2.0. Consequently, the reaction of the positively charged collagen with the negatively charged tannin particles should exhibit a minimum rate of fixation at pH = 5.0 and an increase in fixation from 5.0 to 2.0. It is rather surprising, however, to find that tannin is fixed on both sides of the isoelectric point of collagen (5.0) since it has been generally conceded that tanning could take place only in acid solution. Moeller<sup>28</sup> reported that adsorption of quebracho extract by hide powder was increased when acid was added to the tanning solution, but that practically no adsorption took place in alkaline solution. In the discovery by Wilson and Gallun<sup>16</sup> of two points of minimum swelling for calfskin, at pH = 5.0 and 7.7, respectively, we have a possible explanation of fixation through part of this alkaline range. Assuming two forms of collagen and an intramolecular change in this region resulting in an equilibrium between the one form, A, stable in acid solution and with an isoelectric point at pH = 5.0, and the other form, B, stable in alkaline solution and with an isoelectric point at pH = 7.7, it follows that, with increasing amounts of B, positively charged, in the solution, as the pH increases from 5.0 to 7.7 reaction will naturally take place at an increasing rate with the negatively charged tannin particles. The Procter-Wilson theory furnishes, therefore, a satisfactory working hypothesis for tannin fixation in the pH range from 2.0 to 7.7.

It is to be noted, however, that beyond the maximum points of fixation at pH of approximately 2.0 and 7.7, respectively, the curves show clearly that very definite tannin fixation has taken place, although there is considerable falling off in the rate of tanning. The Procter-Wilson theory fails to account for fixation at these extremes of pH, since the electrical charges on the collagen and tannin particles are identical in sign in these areas, both being positively charged at a pH below 2.0, and both being negatively charged at a pH above 8.0. The question arises whether this fixation is not merely an apparent one, due to change in pH during washing of the tanned powders with distilled water, whereby the tanning solution might have been fixed through removal of acid or alkali by the distilled water before being completely removed itself; but this question has been effectively answered by several experiments in which both tanning and washing solutions were at identical pH values, as shown below.

Experiments were run in which 2,000-gram samples (dry basis) of hide powder were tanned for 24 hours with 100-cc. portions of tanning solution of definite pH. The tanned powders were then transferred to the Wilson-Kern extractors and each sample was washed with a buffer solution, whose pH, by electrometric titration, had been made identical with that of the original tanning solution, this washing being

continued until uncombined tannin had been completely removed, as evidenced by a negative gelatin-salt test on the filtrate. The washing was then continued with distilled water until the buffer solution, in turn, had been completely removed, as well as non-tans. The samples were finally dried and weighed in the usual fashion for determination of tannin fixed.

Results of the average of two duplicate sets of values obtained by this method are recorded in Table IV and Fig. 4, and the average values for tannin fixed are given, together with the corresponding values obtained in an earlier experiment where the washing was done with distilled water in the usual fashion.

TABLE IV—EFFECT OF NATURE OF WASHING SOLUTION

pH of Tanning Solution	WASHING SOLUTION EMPLOYED	GRAMS TANNIN FIXED BY 2 GRAMS HIDE POWDER WASHED	
		With Buffer Solutions	With Distilled Water
1.0	HCl (approx. 0.1 M)	0.613	
2.0	HCl (approx. 0.01 M)	0.790	0.812
3.0	HCl (approx. 0.001 M)	0.742	0.686
4.0	HCl (approx. 0.0001 M)	0.458	0.466
5.0	Mixtures of M/15 primary potassium and secondary sodium phosphates	0.478	0.330
6.0		0.476	0.495
7.0		0.417	0.520
8.0		0.409	0.519
9.0		0.400	0.438
10.0	NaOH (approx. 0.001 M)	0.362	0.346

Since a comparison value at pH of 1.0 was lacking in this set, the following values were obtained, using wattle bark extract at pH of 0.9, the values being run in duplicate:

TABLE V—EFFECT OF NATURE OF WASHING SOLUTION

WASHING SOLUTION EMPLOYED	Grams Tannin Fixed by 2 Grams Hide Powder
Distilled water	0.987
HCl (pH = 0.9; approx. 0.1 M)	0.739

An examination of these results shows that the curves obtained upon washing with buffer solutions parallel closely the one obtained upon washing with distilled water in the range from pH of 2.0 to 4.0, where hydrochloric acid of low concentration was employed, and again at pH of 10.0, where 0.001 M sodium hydroxide was used. At pH of 1.0, where the concentration of hydrochloric acid used for washing was approximately 0.1 M, the fixation was slightly lowered, but real values, both for hemlock and wattle extracts, were obtained for tannin fixed. In the range from 5.0 to 9.0, where mixtures of M/15 phosphate solutions were used in washing the tanned powders, the variations from the normal pH curve are merely due to a salt effect, showing an increase in fixation at pH of 5.0, and a decrease from pH of 7.0 to 9.0, similar in every way to the changes produced where salts are added to the tanning liquors prior to addition to the hide powders, which will be discussed in a separate paper.

It can safely be concluded, therefore, that the fixation of tannin at pH values of 1.0 to 2.0, and 8.0 to 10.0 is a real and not an apparent one, and consequently that some other factor, possibly oxidation reactions, in addition to the co-precipitation of oppositely charged colloidal particles, contributes to the fixation of vegetable tannins by collagen.

Evidence for a difference in kind of fixation of tannin in alkaline solutions as compared to that in acid solutions, shown by alcohol extraction of the tanned leathers, will be described in a later paper.

#### TIME FACTOR IN FIXATION OF TANNIN

From the foregoing tables and graphs, the effect of the time factor on fixation of tannin by hide powder may be observed. The time effect may be best studied with the family of curves obtained with hemlock extract, where the fixation from the more dilute solution, with changing pH, was studied for time intervals of 6 hours, 24 hours, 2 weeks, and 21.5 weeks. The characteristic minimum at pH = 5.0, obtained in the shorter periods, is gradually eliminated, being hardly noticeable in the 2 weeks' tanning period and

completely disappearing in 21.5 weeks. The amount of tannin fixed is always greater with increasing time, but while the minimum at 5.0 disappears, the maximum at 2.0 to 3.0 is steadily maintained, thus indicating that not only is fixation of higher rate at this optimum acidity, but of higher absolute attainment as well. From the data given in Table III it is evident that equilibrium has almost been reached in 21.5 weeks at pH of 2.0 and 10.0 to 11.0, but has been only approximately attained at the other pH values. Furthermore, it is interesting to observe that, with the more astringent extracts, the flat type of pH curve is reached in dilute solution in a fairly short tanning period—e. g., 2 weeks with quebracho.

The question as to the extent to which hydrolysis may have been responsible for the curves has also been investigated. For a tanning period of 24 hours, analysis of the original extract and of aliquot portions of the filtrate for nitrogen by the Kjeldahl method showed no hydrolysis at pH = 1 to pH = 8, a trace at pH = 9, and 1.7 per cent hydrolysis of the hide powder at pH = 10. For the 21.5-week period, with the less concentrated hemlock extract, in which hydrolysis would have most opportunity to show its effect, a similar analysis of the filtrates showed that only at the extremes of pH (1.0 and 11.0) was there sufficient hydrolysis to account for the drops in the curve, as follows:

pH of tanning solution	1.0	3.0	5.0	9.0	11.0
Per cent hydrolysis	20.6	0.29	0.18	1.86	4.22

It is apparent that except for the extremes of acidity or alkalinity in the long time experiment above, the question of hydrolysis affecting the results reported may be excluded as of no significance.

#### ACKNOWLEDGMENT

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consistency was measured by an improved instrument of the Lipowitz<sup>9</sup> type. The solution was placed in a closed jar 4 x 1.5 inches, and set in the cooler at 5° C. for 24 hours. The pressure necessary to force a 3/8-inch glass rod through the surface was measured and this expressed as grams.

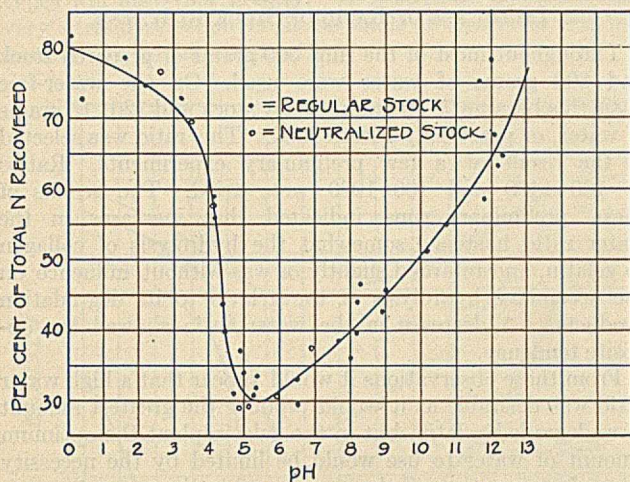


FIG. 1—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF THE TOTAL NITROGEN RECOVERED IN THE SOLUTION

#### VARYING HYDROGEN-ION CONCENTRATION

In the first series the solutions added to the stock consisted of dilute hydrochloric acid, water, and sodium hydroxide of such concentrations that the final solution as recovered varied in H-ion concentration from pH 0.1 to pH 12.4. About thirty-five runs were made, so that the interval in pH between different runs was in all cases slight.

In Figs. 1 to 5 are plotted the curves for the several determinations. In each case the pH is indicated on the abscissa. The ordinates represent, in Fig. 1, the percentage of the total nitrogen recovered in the solution; in Fig. 2, the percentage of the total nitrogen evolved as ammonia; in Fig. 3, the percentage of the nitrogen of the solution which is in the form of terminal amino groups; in Fig. 4, the viscosity of the solution at 35° C. expressed in seconds of outflow through an Ostwald viscometer; and in Fig. 5, the jelly strength of the gel at 5° C. in grams.

<sup>9</sup> Bogue, "Chemistry and Technology of Gelatin and Glue," 1922, p. 371. McGraw-Hill Book Co., New York.

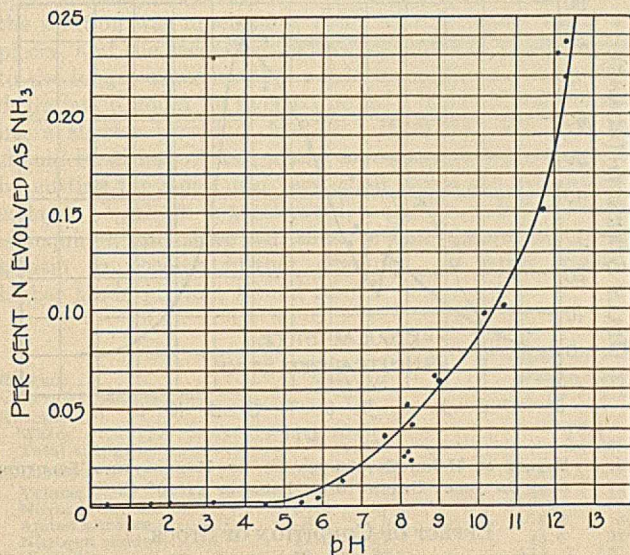


FIG. 2—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF NITROGEN EVOLVED AS NH<sub>3</sub>

The figures bring out a few points which should be emphasized. In the first place, there is a great deal of fluctuation from the mean curves which may be drawn from the data. A single test at any point means very little, and it is only by the accumulation of a considerable number of analyses that we are permitted to draw representative curves. This is due to the irregularity, in spite of care in selection, of the stock employed, and of its water and nitrogen content. But from the large number of data in hand we are justified in making specific conclusions.

Fig. 1 shows that when the concentration of acid in the hydrolyzing mixture is such as to bring the acidity of the final solution to about pH 5 or 6, the hydrolysis is least, only about 30 per cent of the nitrogen of the stock passing into solution under the conditions of the experiment. At slightly stronger concentrations of acid the hydrolysis increases markedly, and it also increases, but less rapidly, with increasing alkalinity.

Fig. 2 shows that up to a pH of 5.4 there is practically no evolution of ammonia, as of course would be expected, but that above pH 5.4 ammonia is evolved in amounts increasing rapidly with the alkalinity of the solution.

Fig. 3 indicates the extent of the secondary hydrolysis—namely, the breaking down of the gelatin molecule into its degradation products, proteose, peptone, and amino acids. Throughout the range of pH 3 to 8 this secondary hydrolysis is slight, but beyond either of these limits, and especially at moderately high alkaline concentration, as pH 12, it becomes very important.

The variation in viscosity with pH of hydrolyzing solution is shown in Fig. 4. There is indicated a distinct minimum at pH 4.7 and a maximum at pH 7.5 to 8.0. There is also a lesser high point at pH 4.1.

The jelly strength curve shown in Fig. 5 is very similar to the viscosity curve.

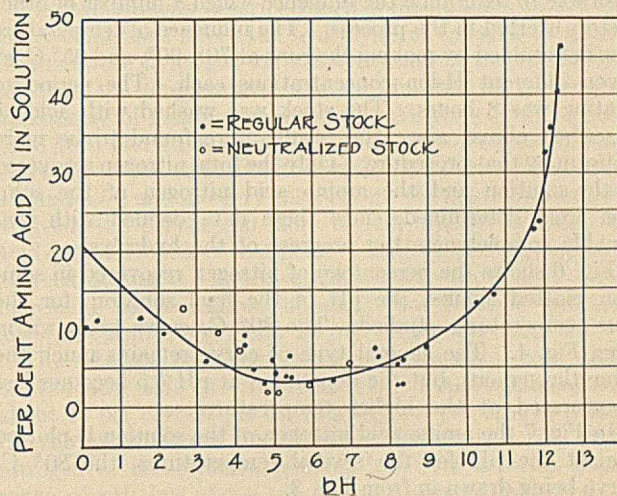


FIG. 3—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF AMINO ACID NITROGEN RECOVERED IN THE SOLUTION

#### INFLUENCE OF SALTS

It seemed possible that the excess of lime which remained in the stock after the washing as usually carried out might influence the results, and a number of runs were made following a special preliminary treatment. The stock was first washed several times with cold water, and then placed in a ball mill with a solution of about 0.01 *N* hydrochloric acid. This washing was followed again by a washing in water. This left the stock practically neutral, as shown by the fact that an hydrolysis in pure water gave a final solution of pH 6.9.

Different amounts of concentrated hydrochloric acid were then introduced into hydrolyzing solution and runs made as before. There was no observable variation in the resulting data until the acidity of the final solution showed a pH of about 4.1. From pH 4.1 to pH 2.6 the solution showed a higher viscosity and jelly strength than the previous tests of similar acidity, but the amount of nitrogen recovered and the degree of the secondary hydrolysis were not noticeably altered. Ammonia was not determined in this series.

The difference in the curves for viscosity and jelly strength are shown by the dotted lines in Figs. 4 and 5.

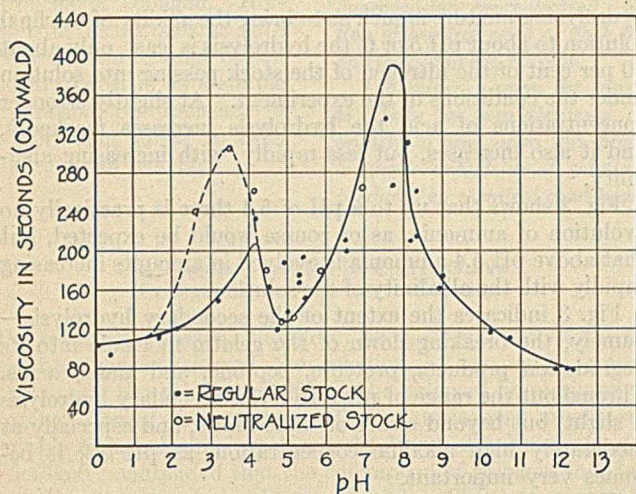


FIG. 4—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON VISCOSITY OF PRODUCT AT 35° C.

#### INFLUENCE OF TEMPERATURE

Having established the general direction and nature of the several curves illustrative of the hydrolysis, it seemed very desirable to determine the influence which a number of other factors exerted in the process. The influence of temperature was determined by making the runs at 70°, 90°, and 95° C. at seven different H-ion concentrations each. The period of heating was 8 hours. The stock was washed with acid as described above, since the results were found to be more uniform by that procedure. Only the total nitrogen recovered in the solution and the amino acid nitrogen of the solution were determined, since these data defined with reasonable completeness the progress of the hydrolysis.

Fig. 6 shows the percentage of nitrogen recovered in solution plotted against the pH of the final solution, for the four temperatures studied. The 80° C. curve is drawn in from Fig. 1. The general type of curve remains much the same throughout, but the depression at pH 5.5 becomes less exaggerated at the higher temperatures.

In Fig. 7 the amino acid nitrogen of the solution is plotted against the pH for the several temperatures, the 80° C. curve being drawn in from Fig. 3.

#### INFLUENCE OF PERIOD OF HEATING

A series of runs was made at seven different H-ion concentrations, tests being made for total nitrogen recovered in solution and amino nitrogen of the solution at intervals of 6, 12, 24, 72, and 168 hours. The temperature was in all cases 80° C. Fig. 8 shows the curves for the nitrogen recovered in solution plotted against the pH of the final solutions for the several periods of heating. The curve for the 8-hour period is drawn in from Fig. 1. At 72 hours the curve is nearly straight, but at 168 hours a depression occurs on the alkaline side. This is probably due to the loss of an appreciable quantity of nitrogen as ammonia under those conditions.

In Fig. 9 the amino acid nitrogen of the solution is plotted against the pH for the several periods of heating, and the

curve for the 8-hour period drawn in from Fig. 3. At 72 hours from 70 to 80 per cent of the nitrogen of the solution is amino acid nitrogen, and at 168 hours it reaches its maximum at 92 per cent and drops on the alkaline side. This drop is also probably due to the formation of ammonia.

#### INFLUENCE OF RATIO OF STOCK TO WATER

Throughout most of the runs 500 grams of prepared stock and 800 grams of water were used. On the water-free basis this became 98.85 grams of dry stock and 1201.15 grams of water, or practically 100 to 1200. This ratio was selected as the result of a few preliminary experiments. Ratios of 100:1400 and 100:1000 were tried. The results of these preliminary runs indicated that increases in the water ratio hastened somewhat the hydrolysis of collagen to gelatin, and retarded slightly or was without influence on the secondary hydrolysis of the gelatin to its degradation products. A decrease in the water ratio showed the opposite tendency.

From these observations it would appear that a high water ratio was desirable as it would produce the greatest amount of undegraded gelatin, but in the gelatin plant the optimum amount of water to use would be limited by the necessity later of evaporating off the excess, and in the present experiments it was desired to obtain a test for jelly consistency, and this would not have been feasible with the 100:1400 ratio. The 100:1200 ratio was very satisfactory from this point of view, while the 100:1000 runs showed a smaller recovery of nitrogen in the solutions, and a slightly greater secondary hydrolysis. The 100:1200 ratio was, therefore, adopted for this investigation.

#### EFFECT OF AGITATION

A few tests were made to determine the effect which agitation would produce on the hydrolysis. This was accomplished by blowing air through the hydrolyzing mixture. The air was first passed through potassium hydroxide, then through water at 80° C., and then into the stock solutions. Four different rates of flow were used, designated as rapid, medium, slow, and zero. The rapid was about ten bubbles per second; the medium, about four; and the slow, about one.

The results indicate that a rapid agitation hastens the primary hydrolysis of collagen to gelatin, but is without influence on the degradation of the gelatin. A rate of about two bubbles per second was employed throughout most of the experiments in this investigation.

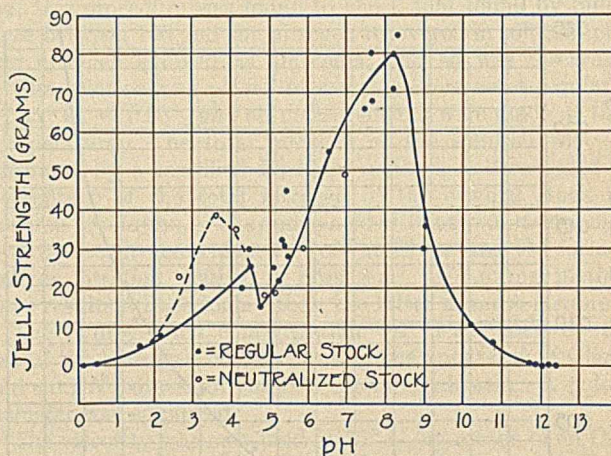


FIG. 5—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON JELLY STRENGTH OF PRODUCT AT 10° C.

#### EFFECT OF CONDITION OF STOCK

A casual inspection of any lot of hide stock for manufacture into glue will show that it is of very un-uniform material.



Some of the pieces will be very thick and firm, others thin and limp. There will be a heavy layer of porous fatty material on the flesh side of some pieces and none on others. Some pieces will be covered with hair and other pieces will be entirely free of hair. The moisture content of these several types will also vary greatly. It is obvious, therefore, that very careful selection must be made if results of fair uniformity are to be obtained.

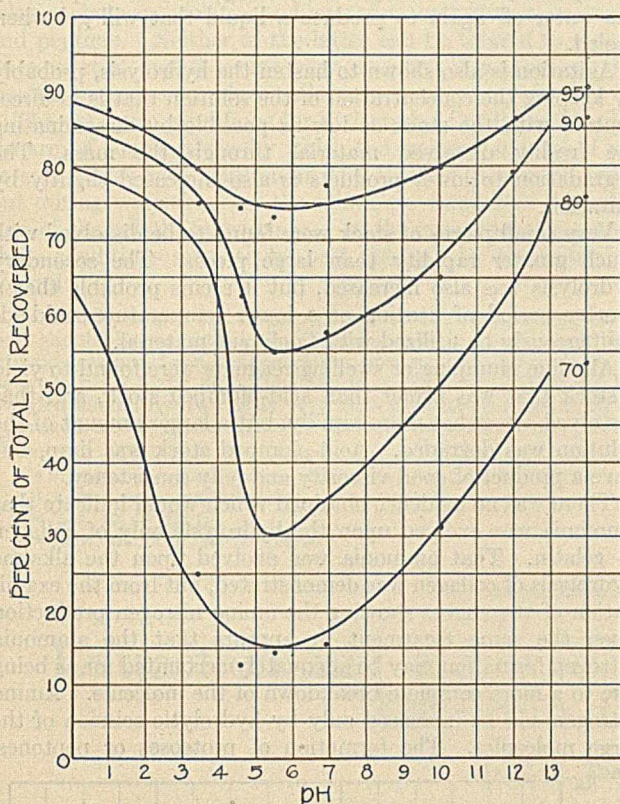


FIG. 6—INFLUENCE OF TEMPERATURE ON TOTAL N RECOVERED IN THE SOLUTION AT VARYING pH

The size to which the pieces were cut for the hydrolysis was found to influence greatly the rate of the reaction. Runs were made using large, thick pieces; strips about 2 inches long by  $\frac{1}{2}$  inch in width and thickness; and pieces cut to approximately  $\frac{1}{4}$ -inch cubes. The recovery of nitrogen in the solution was much more rapid with the more finely cut pieces, and the secondary hydrolysis was also greater owing to the longer exposure of the gelatin produced. This latter degradation could be averted largely, however, by employing a shorter period of heating. It would seem that this should be of importance in the manufacturing processes, for by cutting the stock into very small pieces the hydrolysis of collagen to gelatin is accelerated, a shorter period of heating is required, and there will then be less opportunity for the gelatin to become further degraded. A larger yield of higher grade product should result.

### THE PLUMPING REAGENT

The rate with which the collagen passes into solution is dependent in large measure upon the treatment which it has received prior to the hydrolysis. As a result of a series of swelling experiments, five reagents were selected as of especial merit, and the hide pieces swollen in them were subjected to hydrolysis and several tests made on the resulting solutions. The results are tabulated in Table I.

The water content of the dry, salted stock before treatment of any kind was 34 per cent. After thoroughly washing, during which process the salt, dirt, hair, etc., were removed (amounting to 33 per cent of the dry matter of the stock), the stock contained 70 per cent of water. As will be seen from the table, the water content was raised from 70 to 89 per cent in the lime solution, to 86 per cent in the lactic acid solution, and to lesser amounts in the others. But although the water content of the lime and lactic acid-swollen stock was about the same, their physical conditions were quite different. The former was firm and showed what might be called turgor. The latter was very limp and water could be easily squeezed out of it.

The lime-soaked stock gave the highest yield of nitrogen in the solution, and a moderate amino acid content. The highest viscosity and swelling were obtained with the borax, and the lowest amino acid content with the lactic acid. These irregularities may be in part due to the fact that equal weights of the swollen stock were employed in the hydrolysis rather than weights which would be equivalent on the dry basis. In general, however, the alkaline swelling reagents yielded a product that was firm and went most easily into solution, but the excessive hydrolysis into amino acids was more pronounced than in the acid-swollen stock. The latter was limp but gave solutions of good viscosity and jelly consistency.

### GENERAL DISCUSSION

The experiments described in this report have shown that many conditions affect the hydrolysis of collagen to gelatin. Of these, the hydrogen-ion concentration of the hydrolyzing solution, the temperature, and the duration of heating are apparently of greatest importance. All the curves recorded have been plotted against pH, and in all cases a minimum is observed in the region of the isoelectric point (between pH 4.5 and 5.5), and in every case, except the curve for ammonia evolved, the curves rise more or less rapidly on either the acid or alkaline side of that point. In the case of the ammonia evolved during the hydrolysis, the curve rises rapidly upon increasing concentrations of alkali, but remains uniformly low (practically negligible) at pH values less than 5.0.

The nitrogen recovered in the solution rises very rapidly on the acid side of the isoelectric point, increasing from about 30 per cent at pH 5.0 to about 70 per cent at pH 3.5. On the alkaline side the change is less rapid. The amino nitrogen of the solution remains low over a much greater range of pH, but above pH 9.0 this form of hydrolysis increases very rapidly.

The viscosity and jelly strength curves are nearly parallel and show two maxima, one on the acid and the other on the

TABLE I—EFFECT OF PLUMPING REAGENT ON HYDROLYSIS

Reagent.....	Ca(OH) <sub>2</sub>		MgCO <sub>3</sub> +NaOH		Lactic Acid		Borax		Boric Acid		
Concentration, per cent.....	5		5 + 0.2		1		5		5		
Stock:											
Water.....	89.0		78.1		86.0		80.0		77.5		
Total nitrogen.....	14.09		14.21		14.13		14.00		14.08		
SOLUTION:	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	
Volume.....	1200	1200	1200	1250	1050	1050	1000	1000	1000	1000	
Nitrogen in solution.....	82.4	82.3	76.4	77.2	70.6	67.1	78.8	74.6	71.3	72.5	
Amino nitrogen.....	5.4	5.4	8.2	8.3	3.8	3.6	5.1	4.8	3.9	4.0	
Nitrogen residue.....	17.6	17.7	23.6	22.8	29.4	32.9	21.2	25.4	28.7	27.5	
Viscosity.....	85	86	115	107	148	126	128	135	105	114	
Jelly strength.....	Liquid	Liquid	25	21	22	18	25	29	20	24	
pH.....	9.2	9.2	8.8	9.0	4.2	4.2	7.9	7.9	4.9	5.0	

alkaline side. The depressing effect due to the presence of salts (of calcium) in solution is shown especially well by these curves, for on the acid side much higher maxima come at about pH 3.5 and 8.0.

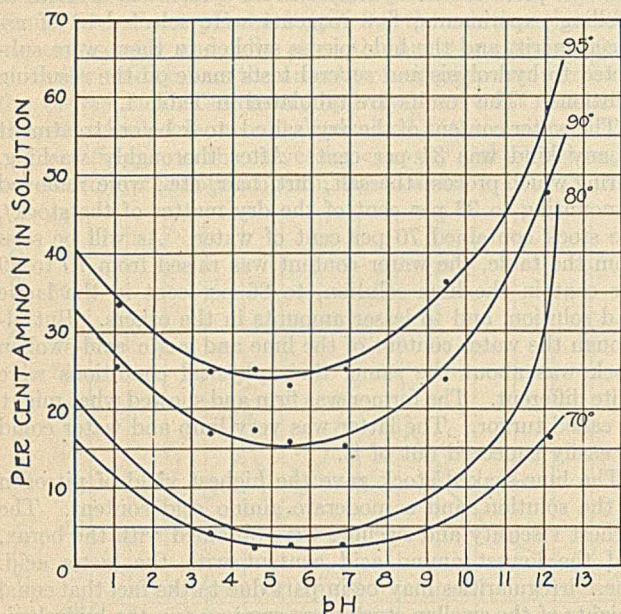


FIG. 7—EFFECT OF TEMPERATURE ON AMINO N IN THE SOLUTION AT VARYING pH

An increased temperature and a lengthened period of heating produce, throughout the entire range of pH, an increased hydrolysis both of collagen to gelatin (as shown by the nitrogen recovered in the solution) and of gelatin to its degradation products (as shown by the amino nitrogen of the solution). At very long periods of hydrolysis (168 hours), however, there appears on the alkaline side a drop in the nitro-

gen recovered in the solution. This is very probably due to the increased loss of nitrogen as ammonia under these conditions.

Theoretically, the most favorable results will be produced by a high ratio of water to stock, for, the concentration being less, it is shown that more of the stock will go into solution during a given period, and this will be degraded to a lesser extent than if concentrated, but, practically, a limit is set to the optimum dilution by the necessity later of evaporating the water off again to produce a liquid that will gel when cooled.

Agitation is also shown to hasten the hydrolysis, probably by keeping the concentration of the solution that is in direct contact with the stock as low as possible by disseminating the freshly dissolved material through the mass. The degradation to lower products is also increased slightly by agitation.

Very small pieces of stock were found to be dissolved with much greater rapidity than large pieces. The secondary hydrolysis was also increased, but it seems probable that a shorter period of heating or a lower temperature could advantageously be utilized with finely cut material.

Alkaline plumping or swelling reagents were found to yield a stock that was firmer than acid-plumped stock, and that dissolved somewhat more rapidly, but a larger amount of the solution was degraded. Acid-plumped stock was limp, but gave a product of good viscosity and jelly consistency.

There was no evidence obtained which would indicate that ammonia was evolved upon the hydrolysis only of collagen to gelatin. That ammonia was evolved upon the alkaline hydrolysis of collagen was demonstrated, but from the examination of the curves showing the amino nitrogen production upon the same treatment, it appears that the ammonia nitrogen formation may be adequately accounted for as being due to a more complete breakdown of the molecule. Amino nitrogen can be increased only by hydrolytic scission of the large molecules. The formation of proteoses or peptones,

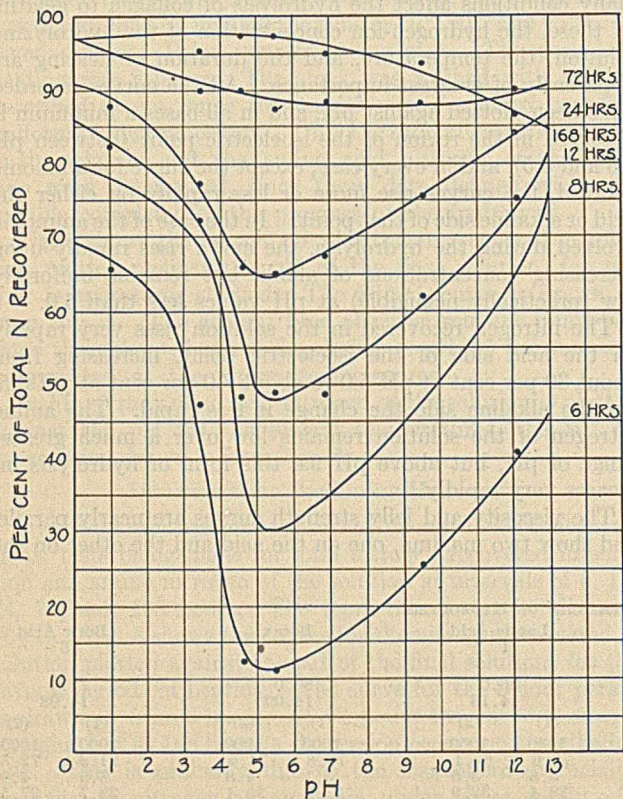


FIG. 8—EFFECT OF PERIOD OF HEATING ON TOTAL N RECOVERED IN THE SOLUTION AT VARYING pH

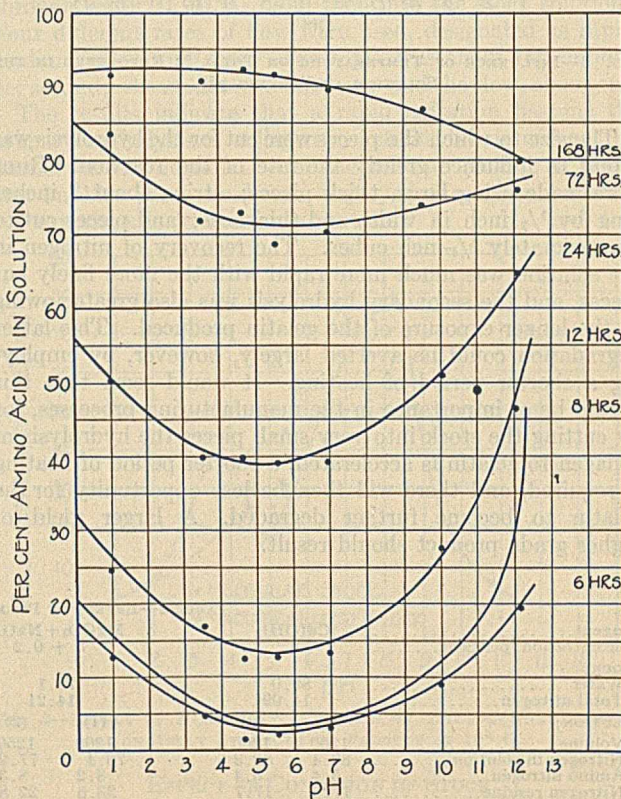


FIG. 9—EFFECT OF PERIOD OF HEATING ON AMINO N IN SOLUTION AT VARYING pH

as well as of free amino acids, increases the amino nitrogen determinable. That this same operation produces also ammonia has been shown in the hydrolysis of gelatin by Fischer,<sup>10</sup> Daken,<sup>11</sup> Van Slyke,<sup>12</sup> Bogue,<sup>13</sup> and others. It seems probable to the writer that collagen is a polymerized complex of gelatin. Upon heating gelatin to 130° C. an anhydride is probably produced, but this is not similar to the original collagen. The polymerization seems to be chemical rather than physical, and would, therefore, be comparable to the relation between gelatin and proteose, or between proteose and peptone. Neither of the latter can be treated to reproduce gelatin, and it seems very doubtful if gelatin can be treated so as to reproduce collagen.

The optimum conditions for hydrolysis of collagen to gelatin are, of course, those by which the greatest amount of nitrogen passes into solution in the shortest period of time, but during which process the minimum amount of degradation of the gelatin takes place. In the experiment reported, these conditions seem to be best attained by the following control:

1—The hydrogen-ion concentration of the hydrolyzing solution should be such that the resulting gelatin or glue solution will possess an H-ion concentration between pH 3.0 and 4.0 or between pH 7.5 and 8.5. The region of pH 4.5 to 6.0 should be avoided as the hydrolysis is very slow at that concentration of hydrogen ions. Above pH 8.5 the degradation of the gelatin

becomes too great, with a corresponding loss of nitrogen as ammonia, and below pH 3.0 there is also a degradation, while in both cases the velocity and jelly strength of the product become very low.

2—A temperature of 80° C. seems most favorable to the hydrolysis of collagen to gelatin, and an 8-hour period of heating is satisfactory. There is too little hydrolysis at lower temperatures or shorter periods of heating (although a somewhat purer product may result under these conditions), while at higher temperatures and longer periods the greatly increased degradation of the gelatin offsets any advantages of more rapid collagen hydrolysis.

3—The optimum ratio of dry stock to hydrolyzing solution (including water in the stock) seems to be about 1:12 or 1:14. Lower concentrations necessitate later evaporation, while greater concentrations give lower yields of gelatin and increased degradation of the gelatin formed.

4—The stock may be swollen in a number of different reagents, lime and lactic acid showing the best results to date, but the excess of reagent should be removed completely by washing and neutralization, as a depressing effect on the viscosity and jelly strength may result from their presence.

5—A fine cutting of the stock and constant agitation are desirable as they make possible a more rapid hydrolysis, but to prevent also a more rapid degradation of the gelatin a shorter period of heating or a lower temperature will be necessary. A 6 or 7-hour heating at a temperature of 75° C. probably will produce, with finely cut stock and thorough agitation, about the same hydrolysis as an 8-hour heating at 80° C. under the opposite conditions.

#### ACKNOWLEDGMENT

The writer wishes to express his indebtedness to C. K. M. Ritchie for performing a number of the determinations reported herein.

<sup>10</sup> Fischer, Levene, and Anders, *Z. Physiol. Chem.*, **35**, 70 (1902).

<sup>11</sup> *J. Biol. Chem.*, **44**, 524 (1920).

<sup>12</sup> *Ibid.*, **10**, 48 (1911).

<sup>13</sup> *Chem. Met. Eng.*, **23**, 156 (1920).

## Extraction and Recovery of Radium, Vanadium, and Uranium from Carnotite<sup>1</sup>

By K. B. Thews and F. J. Heinle

KEYSTONE METALS REDUCTION CO., CHESWICK, PA.

THE carnotite ores now mined in Colorado and Utah are of too low a quality to permit handling and shipping to the reduction plants without first picking out the higher grade ores or else concentrating this ore. The practice in almost all cases is to pick out the higher grade material, which makes it necessary to store in the field large quantities of low-grade carnotite, and it appears that in the future American radium manufacturers will be forced to concentrate all these ores before shipment to the plants is profitable. For this reason, the writers have described in detail the extraction of the values from concentrates instead of ores, and have only mentioned the advantages occurring in extracting the values from ores.

### RADIUM EXTRACTION AND RECOVERY

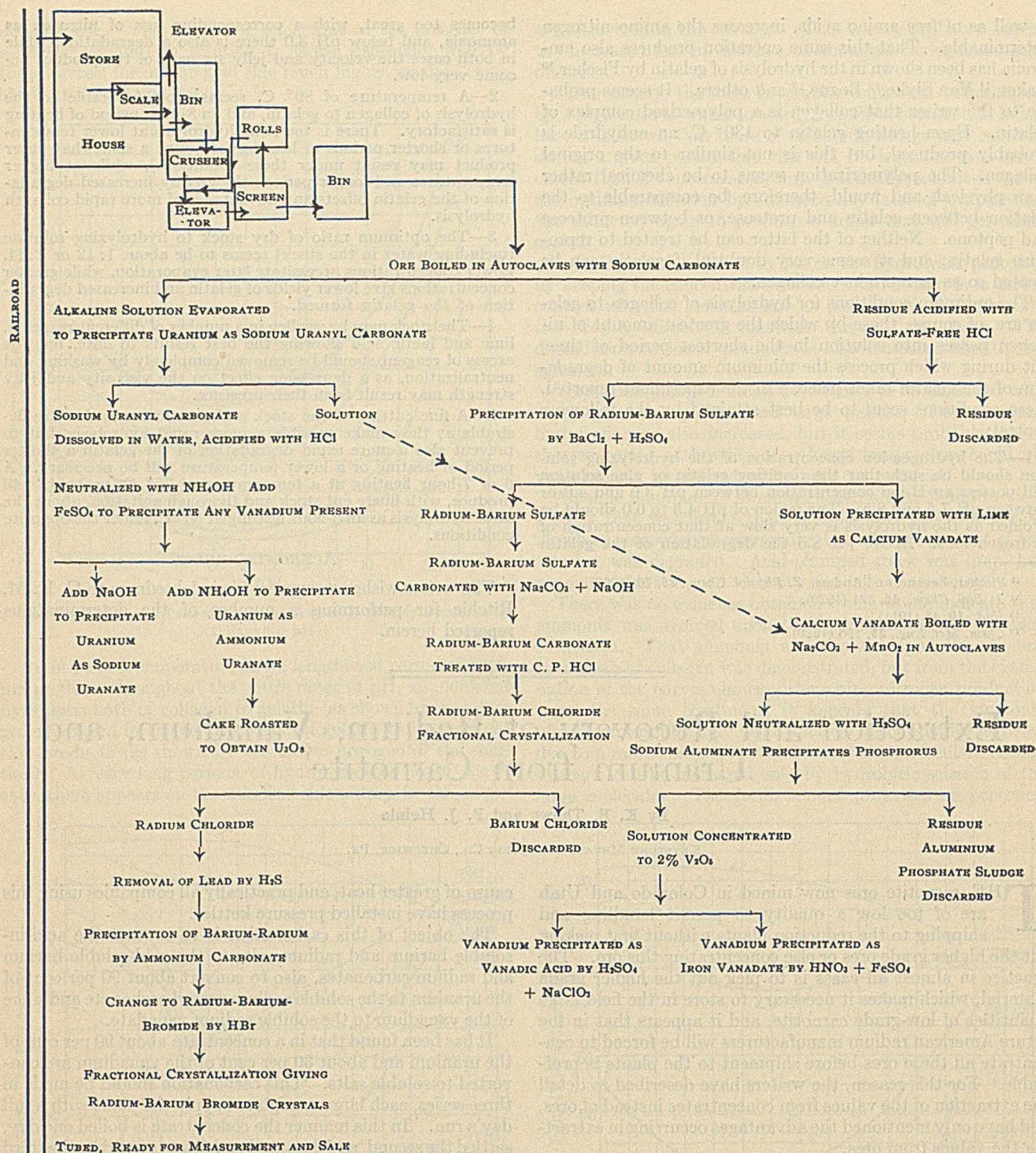
In iron tanks or pressure boiling kettles the following mixture is made—2 parts water, 1 part concentrates, and approximately 200 pounds of soda ash for each per cent of uranium oxide present. This mixed mass is boiled with continuous stirring for from 6 to 10 hours. Should this boiling be done in an open tank and coils used for heating, a small amount of the condensed steam should be returned into the boiling tank to take care of the evaporation of the water. Otherwise, the mass would boil down to the concentration point of soda salts, which would result in the crystallizing out of the uranium salts as the sodium uranyl carbonate. A more complete conversion is made in pressure kettles be-

cause of greater heat, and practically all companies using this process have installed pressure kettles.

The object of this carbonation is to convert the acid-insoluble barium and radium salts to the acid-soluble barium and radium carbonates, also to convert about 90 per cent of the uranium to the soluble sodium uranyl carbonate and some of the vanadium to the soluble sodium vanadate.

It has been found that in a concentrate about 90 per cent of the uranium and about 30 per cent of the vanadium are converted to soluble salts. This carbonation should be made in three series, each large enough to supply the plant with a full day's run. In this manner the concentrate is boiled one day, settled the second, and decanted and filter-pressed on the third day. After decantation the mass is pumped into a washing type, iron filter press and the cake washed with sulfate-free water until the resulting filtrate is free from sulfate. From 6 to 10 hours are required to accomplish this washing. All the decanted liquor, filtrate from press, and part of the wash water containing the soluble vanadium and uranium salts are pumped into evaporating tanks (recovery later), and the remaining wash water is used as mix for new conversions. The cake in the filter press containing the radium is carefully taken out, broken up with about 20 per cent of sulfate-free water in a paddle tank, and pumped into the acid-treating tanks. These tanks resist the action of the acid and are so constructed that the mass can be stirred well. Enough sulfate-free hydrochloric acid is added to neutralize all carbonates, etc., and to acidify the solution. A solution of 2 per cent

<sup>1</sup> Received June 28, 1923.



FLOW SHEET OF RADIUM PROCESS

acidity is generally sufficient for this purpose. The acid-consuming number can be easily found by taking a 100-gram sample of the carbonated cake, acidifying, and boiling it with a given quantity of hydrochloric acid and then titrating the filtrate with a normal caustic solution. The excess needed can then easily be calculated. The acidified mass, in tanks, is then boiled for 20 to 60 minutes and pushed into washing-type, wooden filter presses, by means of a blow case, and washed with sulfate-free water until the resulting wash waters are barium-free. The filtrate and wash waters will now contain over 90 per cent of the radium and about 80 per cent of the vanadium not taken out by the carbonate conversion. The cake in the filter press is free from radium,

vanadium, and uranium and can be discarded. The filtrate wash waters are run into large boiling tanks and the radium is precipitated with sulfuric acid, or a soluble sulfate, such as sodium acid sulfate. In case no barium has been introduced, a small quantity (about one-half pound) of barium chloride per milligram of radium present is added before this precipitation is made. The precipitated radium barium sulfates are left to settle for from 2 to 4 days, when most of the liquor containing the vanadium is decanted off, and the remaining liquor plus the precipitated sulfates dropped on vacuum filters and the liquor separated from the cake. This radium barium sulfate will contain about 1200 milligrams per ton; therefore, a concentration of 1 to 100 or more has been made.

The cake containing all the radium and barium as sulfates is washed and mixed in an autoclave with two parts of its dry weight of soda ash, 10 per cent caustic soda, and four parts of water, and boiled for about 12 hours. The radium barium carbonates resulting from this conversion plus liquors are pumped into a small, washing type, iron filter press, and washed sulfate-free with distilled water. The cake containing the radium and barium is taken out carefully and treated with C. P. hydrochloric acid. After filtering, the radium in the filtrate is ready for fractional crystallization. This is done by either the neutral or acid method of crystallization. Since many publications have been written on the fractional crystallization of radium, the writers will not describe it in this paper.

#### PLANT CONTROL OF RADIUM

Chemical plant control is a very important factor and is carried out with great care. Possible contaminations by sulfates must be guarded against and eliminated, and since the ore contains sulfates and sulfuric acid is used in the process, contaminations are easily possible. Rapid qualitative tests for sulfates are made repeatedly, especially after the carbonate conversions and before the hydrochloric acid treatment. The hydrochloric acid treatment department is generally kept away from the other departments for this reason, and all operators are warned to keep clothing such as shoes, etc., in clean condition. At this point sulfates will do most of the damage. Should sulfates enter, reprecipitate some of the radium to insoluble sulfate, a costly reconversion with sodium carbonate is necessary.

#### EXTRACTION FROM ORES

Most of the radium plants today do not concentrate their ores but resort to hand picking and shipping this picked ore to their plants. In this case the ore is first crushed and ground to from 20 to 30-mesh before the values are converted with sodium carbonate, and after the first hydrochloric acid treatment the slimes and liquors are decanted off and pumped into filter presses. Since the average ore, after crushing, consists of about 15 per cent of slimes and 85 per cent sandy material, and since the sands after acid treatment contain practically no radium, this decantation results in a considerable saving in labor and equipment. A few washes after the main liquor has been decanted off will free the sands from all values. Otherwise, ores are treated the same as concentrates.

#### URANIUM RECOVERY

The liquor from the first carbonation, containing about 90 per cent of the uranium and some of the vanadium, is pumped into large tanks and evaporated until the concentration point of the contained soda ash is reached. This point can be ascertained by blowing a film on the top of a sample taken from the solution. At this point all the uranium crystallizes out as the sodium uranyl carbonate, and the vanadium remains in the liquor. The mass is filtered and the sodium uranyl carbonate slightly washed with cold water. The sodium uranyl carbonate is dumped into a wooden tank and enough water added to dissolve the salt. The mixture is then slightly acidified and boiled to drive off all carbonates and almost neutralized with ammonia. A little vanadium is carried along with the uranium, and for the purpose of eliminating this vanadium a small quantity of ferrous sulfate is added. After the iron vanadate has been separated from this solution by filtration, the uranium is precipitated with ammonium hydroxide as the ammonium uranate. The precipitated mass is pumped into a washing type, iron filter press and the cake washed until all the soda salts have been removed. The ammonium uranate is put into a roasting furnace and converted to the uranium oxide by heat. A small amount of the ura-

nium will be precipitated as sodium salts, owing to the soda salts present, but it has been found that an oxide of 97 per cent purity can be made. In case a purer salt is wanted the ammonium uranate is redissolved and reprecipitated.

If caustic soda is used after the solution has been freed from the vanadium, sodium uranate is precipitated.

#### VANADIUM RECOVERY

The vanadium in the acid solution decanted from the precipitated barium radium sulfate is pumped into large stirring tanks, boiled, and the vanadium precipitated with lime as the calcium vanadate, filtered, and washed. The cake containing the vanadium is then mixed with the liquor from the sodium uranyl carbonate evaporation plus 10 per cent of sodium carbonate, a small amount of oxidizing agent such as manganese dioxide, and boiled for 2 hours. By adding the liquor from the sodium uranyl carbonate evaporation to the lime cake, vanadium is not only combined, but a considerable saving in soda ash is made. The boiled mass is pumped into washing type, iron presses and the cake washed free of vanadium. About 95 to 98 per cent of the vanadium is now in solution. The cake can be discarded. This solution is pumped into wooden tanks, almost neutralized with sulfuric acid, and the phosphorus from the ore carried along, precipitated with sodium aluminate as an aluminium phosphate sludge. This sludge is filtered off and the solution is pumped into an evaporating tank and boiled until a 2 per cent vanadium solution is reached. This is then precipitated as the vanadic acid by adding a slight excess of sulfuric acid and boiling vigorously. It has been found that sulfuric acid will not precipitate vanadium in weak solution and that when a solution is concentrated to about 2 per cent  $V_2O_5$  content, the most efficient results are obtained. A vanadic acid containing 80 per cent  $V_2O_5$  can be precipitated by this method. This precipitated vanadic acid is filter-pressed, washed free from sulfates, and dried. The resulting vanadium oxide is ready for reduction. In case iron vanadate is wanted, the solution does not have to be evaporated, but is almost acidified with sulfuric acid, and after dephosphorization slightly acidified with nitric acid and the vanadium precipitated with ferrous sulfate. By decreasing or increasing the excess acidity, iron vanadate of various purities can be made. A higher acidity will give a higher grade concentrate.

#### CONCLUSION

The process described has its disadvantages when compared with others such as the nitric acid,<sup>2</sup> sulfuric acid leaching,<sup>3</sup> niter cake fusion<sup>4</sup> processes. It requires more equipment, more careful checking, and the solutions and cakes have to be handled more frequently. Its chief advantage lies in the fact that when operated carefully, purer and more easily worked solutions result. Under normal conditions, recoveries of 80 per cent or better of all values in carnotite are being made. There is very little difference in costs of operation between these processes, so this process is today the most popular one used on carnotite ores.

<sup>2</sup> Parsons, Moore, Lind, and Schaefer, *Bur. Mines, Bull.* 104.

<sup>3</sup> Fleck, Haldane, and White, U. S. Patent 890,584.

<sup>4</sup> Schlundt, U. S. Patent (?).

#### Indiana Section Aids Fire Department

At the request of the chief of the fire prevention division of the Indianapolis Fire Department a committee headed by Cecil Calvert will prepare instructions for the use of firemen when handling fires in which acids or other chemicals that might cause explosions or spread dangerous gases are encountered. The recent unfortunate experience of the Milwaukee department led to the request and the organization of the committee. Possibly other sections may find that they can similarly serve their own communities.

# The Biological and Chemical Significance of Gamma Sugars<sup>1</sup>

By James Colquhoun Irvine

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, THE UNIVERSITY, ST. ANDREWS, SCOTLAND

NO ATTEMPT has hitherto been made to compile a general survey of our knowledge regarding the reactive types of reducing carbon hydrates which are known collectively as gamma sugars. Although these important variations of sugar molecules have been recognized for some years, they present unusual difficulties to penetrative study, and despite laborious research still remain largely obscure and unexplained. Nevertheless, they have recently been invested with a special interest and are referred to with a freedom which displays the necessity to review what is known regarding them.

## REASON FOR NAME

To begin with, the name applied to them is not descriptive, but is, in a sense, accidental. As is well known, the best-defined reducing sugars can generally be obtained in two isomeric forms which display mutarotation in opposite directions, and this is attributed to the rearrangement of the groups in the reducing position. The expressions "alpha" and "beta" were applied to designate these isomerides, and the two mutarotatory forms of glucose serve as standard examples in illustration. Now this isomerism has been proved to be in no way dependent on the position of the internal oxygen ring in the sugar, since both  $\alpha$ - and  $\beta$ -glucose have been correlated with the butylene oxide form of tetramethylglucose. The discovery that another variety of glucose exists, in which the oxygen ring is differently attached, could not be accommodated by the nomenclature then in use and the expression " $\gamma$ -glucose" was applied to it. The name "gamma sugar" has therefore a very general significance and is used to include all forms in which the oxygen ring is displaced from the normal stable position. This is not entirely satisfactory, but a more exact nomenclature cannot be applied until the complete structure of each of these sugars has been established. Meanwhile, it may prevent confusion if it is pointed out that gamma sugars, retaining as they do a reducing group, can exist in alpha and beta modifications, and the same remark applies to their glucosides.

Up to the present it has been ascertained that glucose, galactose, mannose, rhamnose, and fructose are all capable of existing in gamma forms, and there seems no reason to doubt that the property is general. In no case, however, has an unsubstituted gamma sugar been isolated, although we recognize their transient existence, and can in some measure study their properties by examining their methylated derivatives. The presence of the methyl groups in these derivatives prevents any alteration in the oxygen ring, and thus the constitutional type is preserved.

<sup>1</sup> Presented before the Division of Sugar Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

*This article is a brief review of the present knowledge of gamma sugars. The name is applied to all forms of sugars in which the oxygen ring is displaced from the normal, stable position. The discovery of these sugars was the result of gradually accumulated evidence beginning from work by the author on the methylation of sucrose and the separation of the sugars formed on hydrolysis, when it was found that the methylated fructose was dextrorotatory.*

*The reactions show properties entirely different from those of normal sugars. Experiment points to the theory that the natural processes leading to formation of sugars involve the formation of gamma sugars as intermediate stages. It is possible that these are not chemical individuals, but only a condition of the sugar molecule.*

## DISCOVERY

Before summarizing the chemistry of gamma sugars, it may be mentioned that their discovery did not originate in any single dramatic observation, but that the evidence accumulated gradually. One of the writer's laboratory notebooks, describing work carried out exactly twenty

years ago, gives an account of the methylation of sucrose, and the separation of the sugars thereafter formed on hydrolysis. Crystalline tetramethylglucose was isolated and, in addition, the corresponding fructose derivative was obtained by means of condensation with methanol at room temperature, followed by the usual fractional distillation and hydrolysis. The complete analysis of the product was carried out, its composition was ascertained to be that of a tetramethylfructose, and its specific rotation was shown to be of the order  $+27^\circ$ . The entry in the book states that the work was at this stage suspended, there being no adequate explanation as to why a methylated fructose should be dextrorotatory. The compound was, in fact, pure tetramethyl- $\gamma$ -fructose, but many consecutive researches were necessary before the discovery could be interpreted. A subsequent paper on the methylation of fructose added materially to the evidence that the ketose can react in a dextrorotatory form, and about the same time a result of equal significance was forthcoming. A levorotatory trimethylglucose was obtained from glucosemonoacetone, and in investigating the origin of this compound a new levorotatory form of tetramethylmethylglucoside was isolated, thus showing that not only can *d*-fructose react in a *dextro* form, but *d*-glucose can exist in a levorotatory variety.

At this stage Fischer published his paper on  $\gamma$ -methylglucoside, which was quickly followed by our account of the isolation and properties of tetramethyl- $\gamma$ -glucose. In view of this theoretical development, the way was now clear to resume the study of sucrose and to expand the scope of the work.

## PROPERTIES

For reasons already stated, the properties of gamma sugars have to be inferred from those of their methylated derivatives and, so far, the following examples, together with the corresponding methylglucosides, are available for study:

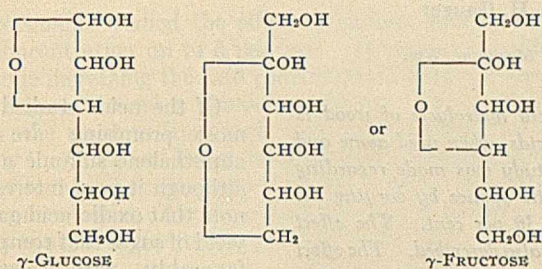
Tetramethyl- $\gamma$ -glucose (levo)  
 Trimethyl- $\gamma$ -glucose (levo)  
 Tetramethyl- $\gamma$ -galactose (levo)  
 Tetramethyl- $\gamma$ -mannose (levo)  
 Tetramethyl- $\gamma$ -fructose (dextro)  
 Trimethyl- $\gamma$ -fructose (dextro)

In reviewing their reactions, one is struck by the close resemblance shown to natural processes. For example, the compounds undergo oxidation with extreme ease, being affected by mild oxidizing agents, and in illustration it

may be mentioned that trimethyl- $\gamma$ -glucose reduces Fehling's solution instantaneously at room temperature. At ordinary temperatures, also, they are converted into glucosides, at a speed which is remarkable, especially when it is remembered that the formation of  $\alpha$ -methylglucoside requires a treatment of approximately 60 hours at 100° C. In at least one case (tetramethyl- $\gamma$ -galactose), a reducing sugar of the gamma type is known to pass spontaneously by autocondensation into a nonreducing disaccharide. These striking properties are far removed from those of a normal sugar.

#### CONSTITUTION

Great difficulties have been encountered in attempts to solve the constitution of gamma sugars, and experimental work has been largely confined to tetramethyl- $\gamma$ -glucose, trimethyl- $\gamma$ -fructose, and tetramethyl- $\gamma$ -fructose. In the case of the glucose derivative, the first opinion formed was that an ethylene oxide ring was present, but this view has been modified in favor of the propylene oxide structure. Similarly, an amylene oxide constitution is at present supported for tetramethyl- $\gamma$ -fructose, so that meanwhile the parent sugars may be represented as:



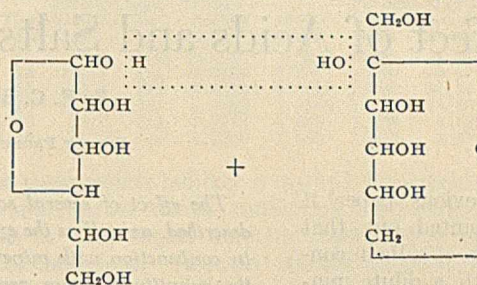
It is already evident that the butylene oxide structure cannot be assumed for any sugar, even in its most stable form. Thus, crystalline xylose, which displays none of the properties of a gamma sugar, has recently been shown to be an amylene oxide, and in this respect at least resembles  $\gamma$ -fructose.

Speculation in the absence of experiment is best avoided in the carbohydrates, but in the course of investigating many varieties of gamma compounds, it was found impossible to reject the idea that the ordinary, crystalline, comparatively stable sugars of the laboratory are not the forms which are primarily elaborated by the plant or disrupted by the animal. The fructose which we store in the chemical museum, and produce as a lecture specimen, is not fructose as it exists in combination in sucrose or in inulin.

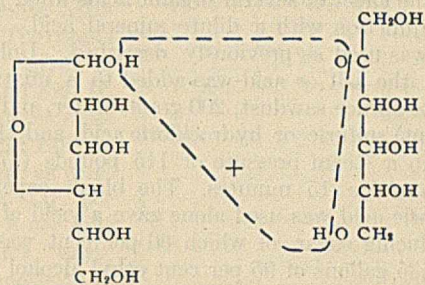
The idea conveyed above is that the natural processes leading to the formation of sugars and their derivatives, as also the ultimate utilization of carbohydrates by the animal organism, involve as intermediate stages the transient formation of gamma sugars. The evidence may not be particularly convincing save to those who have handled all types of carbohydrates at the working bench, but it is certainly true that we have fleeting glimpses of extraordinarily reactive sugars which in the process of artificial isolation from either plant or animal sources undergo rearrangement to the sugars as we know them. This is not inconsistent with the results obtained in either hydrolysis or synthesis effected by enzymes. If this suggestion is substantiated, it may have far-reaching effects in studying physiological processes, and in the treatment of conditions such as diabetes in which the metabolism of sugars is abnormal. Research designed to test this idea was commenced three years ago, and the first tentative steps have been taken to ascertain if living tissue promotes the formation of  $\gamma$ -glucose. The evidence obtained is encouraging, but further progress is hampered by the inaccessibility of gamma sugars, and the lack of trustworthy methods of identifying them. When it is remembered

that  $\gamma$ -glucose and  $\gamma$ -fructose revert instantaneously to their respective stable forms in the presence of 0.1 per cent of hydrochloric acid, it will be agreed that there is little prospect of detecting these fugitive isomerides by ordinary processes. Analytical methods are of no avail, and polarimetric evidence alone is insufficient and often misleading. No doubt these difficulties will be surmounted in time, but only when the detailed chemistry of gamma sugars has been advanced on systematic lines, and when knowledge exceeds impatience.

Having in a sense created gamma sugars for you, it may appear contradictory to say that it is doubtful whether these substances are, after all, chemical individuals. They may only represent a condition of the sugar molecule which originates in the mechanism whereby a sugar forms certain of its derivatives. To make the point clear by means of an example, we need not assume that in the formation of sucrose a molecule of normal glucose condenses with a molecule of  $\gamma$ -fructose in such a manner that each loses a hydroxyl group:



It is possible that  $\gamma$ -fructose may have no real existence, and the condensation may be equally well explained on the assumption that fructose functions as a ketone. In such a case, two hydroxyl groups become involved, and although one of these must be the reducing group of the aldose molecule, there is no reason, once the reaction is initiated, why the ketose itself should not furnish the second group:

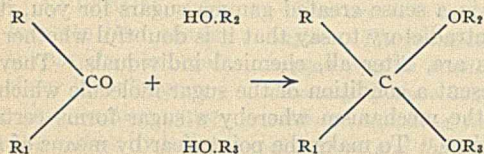


An amylene oxide ring is thus formed in the ketose component and here we see the production of a gamma residue without the previous existence of a gamma sugar. Similar considerations apply to the formation of  $\gamma$ -glucose derivatives which may be formed in condensation reactions in which glucose reacts as an aldehyde. These suggestions are not without the support afforded by numerous analyses, and meanwhile the whole subject is a maze of possibilities, and enlightenment is still remote.

For example, if the question is raised as to why sucrose is so remarkably unstable towards hydrolysis, the existence of an amylene oxide ring in the fructose component provides no answer. Methyl xyloside is likewise an amylene oxide; yet the compound resists the effect of dilute acids, while  $\beta$ -glucosan, which contains a hexylene oxide ring, is notably stable. Again, fructose mono- and di-acetones both undergo hydrolysis with a facility which resembles that displayed by sucrose, but nevertheless both of these compounds are based on the stable type of fructose in which a butylene oxide ring is present. These apparently contradictory results

reveal that the special instability of gamma derivatives does not depend primarily on the presence of any particular internal ring in the sugar.

On the other hand, when aldehydes or ketones condense with hydroxy compounds (including sugars), the products resemble sucrose in their ease of hydrolysis. Numerous isopropylidene and benzylidene derivatives may be quoted in illustration, and the reactions in which such compounds are formed have been shown to follow the course indicated below:



Applying this to the special case of carbohydrates, gamma sugars may be regarded in a new light— $\gamma$ -fructose may, in fact, be nothing more than the ketonic form of the sugar, and  $\gamma$ -glucose the corresponding aldehyde. It may well be that the aldoses and ketoses functioning in their primary capacity as aldehyde and ketone are the reactive sugars in nature, but this much seems clear—no naturally occurring compound of glucose, whether glucoside, disaccharide or polysaccharide, has been found to contain the  $\gamma$ -glucose structure, and the reactive type of the sugar has hitherto been obtained only under artificial conditions. In sharp contrast, the two most important natural derivatives of fructose are each based on  $\gamma$ -fructose, which may possibly prove to be the connecting link in natural processes whereby the interconversion of ketoses and aldoses is effected.

## Effect of Acids and Salts upon the Hydrolysis of Wood<sup>1</sup>

By E. C. Sherrard and W. H. Gauger

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IN A previous paper<sup>2</sup> it was pointed out that the use of salts in connection with a dilute mineral acid gave variable results, and that no close prediction could be drawn regarding the effect of these salts upon the quantity or nature of sugar produced. Since then the effect of a few additional salts has been studied, as well as the effect of several organic acids when used alone and in conjunction with a dilute mineral acid. The same procedure was used as previously described. Unless otherwise noted, the salt or acid was added to a mixture of 100 grams white spruce sawdust, 200 grams water, and 2.5 grams (100 per cent) sulfuric or hydrochloric acid, and the mixture subjected to a steam pressure of 115 pounds (175° C.) in an autoclave for 15 minutes. The blank experiment in which sulfuric acid was used alone gave a yield of 21.14 per cent of reducing sugar, of which 66 per cent was fermentable, or 21.35 gallons of 95 per cent ethyl alcohol per ton of dry wood.

The salts used in this case gave no great variation in yield, as will be noted in Table I.

TABLE I—SALTS

Cook No.	CATALYST	Per cent Reducing Sugar in Terms of Dry Wood	Per cent Fermentable Sugar	Alcohol Gallons per Ton of Dry Wood	REMARKS
74	1.25% BaCl <sub>2</sub> (HCl)	22.70	69.2	22.8	Fermented with difficulty
78	0.5% Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	18.86	38.5	9.0	
79	0.5% K <sub>2</sub> SO <sub>4</sub>	21.50	61.7	19.4	
80	0.5% ZnCl <sub>2</sub> (HCl)	22.58	69.2	21.7	
81	1.25% Ca(NO <sub>3</sub> ) <sub>2</sub>	21.74	67.3	21.0	

Here, as before, no outstanding increases in yields were obtained, although barium chloride and zinc chloride in the presence of hydrochloric acid gave yields slightly greater than were obtained in the blank experiment.

The yields of total reducing sugar and alcohol obtained by the use of different acids are given in Table II.

*The effect of several salts upon the acid hydrolysis of wood is described, as well as the effect of several acids, when used alone and in conjunction with mineral acids. A study was made regarding the quantity of sugar produced from white spruce by varying the concentration of sulfuric acid from 5 to 30 per cent. The effect of time and pressure upon sugar yields is also described. The effect of temperature upon mannose indicates that its rate of decomposition under similar conditions is practically the same as that of glucose.*

Of the acids studied the most promising are the naphthalene sulfonic acids, although it is of interest to note that oxalic acid gave a yield of sugar that compares favorably with those of stronger acids. Trichloroacetic acid gave the poorest results of any of the acids tried.

TABLE II—ACIDS

Cook No.	CATALYST	Per cent Reducing Sugar in Terms of Dry Wood	Per cent Fermentable Sugar	Alcohol Gallons per Ton of Dry Wood
68	1.8% H <sub>3</sub> PO <sub>4</sub> (alone)	16.66	49.00	11.4
69	2.5% H <sub>3</sub> PO <sub>4</sub> (alone)	16.45	51.3	12.3
71	1.8% Cl <sub>3</sub> C—C(=O)—OH (alone)	3.75	No fermentation	
72	2.5% Cl <sub>3</sub> CC(=O)—OH (alone)	2.30	No fermentation	
73	2.5% Cl <sub>3</sub> C—C(=O)—OH (alone)	3.41	No fermentation	
75	0.5% H <sub>2</sub> BO <sub>3</sub>	22.59	63.5	20.5
76	1.7% C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> H (alone)	20.35	55.0	16.6
77	2.5% C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> H (alone)	22.68	56.0	17.4
82	0.5% C <sub>10</sub> H <sub>8</sub> (OH)SO <sub>3</sub> H	23.28	59.9	20.8
83	2.0% C <sub>10</sub> H <sub>8</sub> (OH) <sub>2</sub> (SO <sub>3</sub> H) <sub>2</sub>	24.46	61.4	22.1
84	2.0% C <sub>10</sub> H <sub>8</sub> (OH) <sub>2</sub> (SO <sub>3</sub> H) <sub>2</sub> (alone)	11.14	28.7	4.9
85	1.95% C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> H	23.76	60.3	20.1
86	5% HC(=O)—OH (alone)	12.34	Not fermentable	
87	5% C(=O)—OH (alone)	22.45	58.2	19.7
88	1.25% C <sub>6</sub> H <sub>5</sub> (OH) <sub>2</sub> SO <sub>3</sub> H	22.82	60.0	20.9
89	0.5% C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> )SO <sub>3</sub> H	23.01	63.2	22.1
90	1.25% C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> )SO <sub>3</sub> H	22.88	62.5	21.8

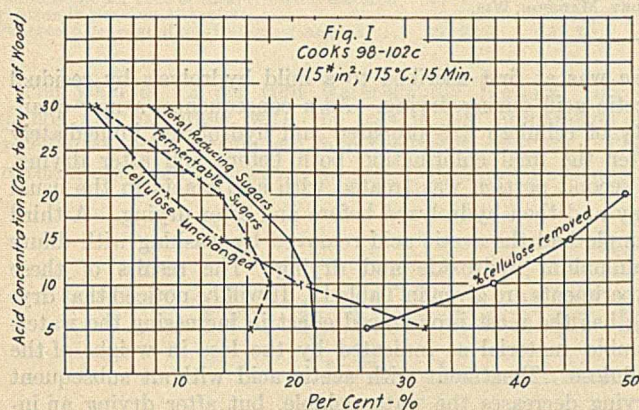
Apparently, the acid decomposed under the condition imposed, for in every case where trichloroacetic acid was used the odor of chloroform was noticed in the digested material.

<sup>1</sup> Presented before the Division of Cellulose Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

<sup>2</sup> THIS JOURNAL, 15, 63 (1923).



No effort was made, however, to identify it accurately. The yields obtained by the use of phosphoric acid were surprisingly low. Kressmann<sup>3</sup> reports a yield of sugar of 19.38 per cent and 15.66 gallons of 95 per cent alcohol per ton. Sulfanilic acid also gave yields somewhat higher than were obtained in the blank.



Kressmann studied the effect of sulfuric acid by varying the concentration up to 5 per cent. It was now decided to continue increasing the acid concentration until the fermentable sugars showed a decided decrease. To complete the study the residues from each cook were analyzed for cellulose by the Cross and Bevan method, in order to determine the extent to which decomposition occurs during the treatment. The concentration of sulfuric acid was varied between 5 and 30 per cent, with the results given in Table III.

Grams of H <sub>2</sub> SO <sub>4</sub> per 100 of Dry Wood	Per cent of Original Dry Wood			
	Total Reducing Sugars	Fermentable Sugars	Cellulose Unchanged	Cellulose Removed
5	21.98	16.29	31.7	26.5
10	21.54	13.00	20.46	37.74
15	19.71	16.10	13.71	44.50
20	16.00	13.67	8.95	49.25
30	7.28	2.70	2.14	56.06

It will be noticed that after a maximum is reached a fairly uniform decrease of total reducing sugars and fermentable sugars occurs, while the cellulose removed increases very rapidly. Since the ratio of sugar to cellulose removed increases with the concentration of acid, it appears that the sugars are destroyed more rapidly than the cellulose is hydrolyzed. These changes are shown somewhat more clearly in Fig. I.

The yield of fermentable sugar having been materially increased by the use of 10 per cent sulfuric acid for 15 minutes, a second set of experiments was run in which the acid concentration was held constant at 10 per cent but the time factor was varied. Here again the yield of fermentable sugars passed through a maximum, although the subsequent drop was gradual. The maximum in this series of experiments came with an acid concentration of 10 per cent and a cook of 10 minutes' duration at 115 pounds' steam pressure (175° C.). The results may be seen in Table IV.

Cook No.	Time Min.	H <sub>2</sub> SO <sub>4</sub> in Pressure Lbs./Sq. In.	Per cent of Dry Wood	Total Reducing Sugars	Per cent Fermentable Sugars	Alcohol Yield Per cent	Gallons Alcohol per Ton of Dry Wood
104c	5	115	10	21.54	13.50	6.88	20.80
105c	10	115	10	23.98	17.02	8.67	26.30
99c	15	115	10	21.54	16.54	8.45	25.60
108c	15	115	10	22.35	16.64	8.47	25.67
106c	20	115	10	21.42	15.85	8.10	24.55
109c	25	115	10	21.92	16.18	8.27	25.05

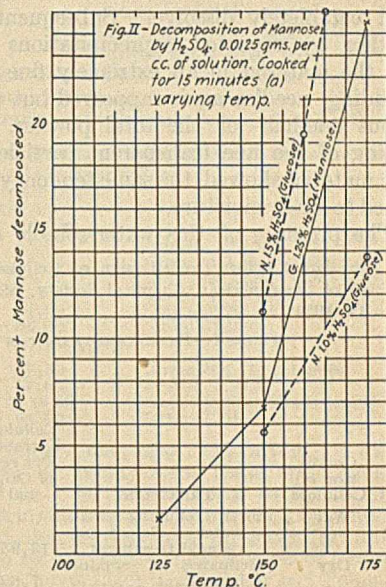
Having varied acid and time factors, the pressure factor was now studied, and a series of experiments was performed

using 7.5 per cent sulfuric acid cooking for 15 minutes and varying the pressure from 80 pounds in Cook 110c to 125 pounds in Cook 116c. This series of experiments gave the highest yields of alcohol obtained heretofore on white spruce sawdust, a yield of 29.05 gallons of 190 proof or 27.6 gallons of absolute alcohol being obtained—a 29 per cent increase over the blank. The results of these experiments are shown in Table V.

Cook No.	Time Min.	H <sub>2</sub> SO <sub>4</sub> Pressure Lbs./Sq. In.	Per cent Wood	Total Reducing Sugars	Per cent Fermentable	Alcohol Yield Per cent	Gallons Alcohol per Ton of Dry Wood
110c	15	80	7.5	21.44	13.40	6.85	20.70
111c	15	100	7.5	22.51	15.12	7.72	23.40
112c	15	120	7.5	23.60	17.80	9.11	27.60
116c	15	125	7.5	22.29	16.05	8.11	24.55

Cook No.	Time Min.	Average Pressure Lbs./Sq. In.	Average Temperature ° C.	H <sub>2</sub> SO <sub>4</sub> Concentration G./Cc.	Per cent Mannose			Undecomposed
					Before Cook	After Cook	Decomposed	
1M	15	19.6	125	0.0125	3.644	3.588	1.54	98.46
2M	15	115.1	175	0.0125	3.752	3.786	-0.91	100.96
3M	15	115.1	175	0.0125	1.9152	1.156	24.55	75.45
4M	10	115.1	175	0.0125	1.9180	1.312	14.50	85.5
5M	15	54.6	150	0.0125	1.882	1.403	6.82	93.18
6M	15	19.6	125	0.0250	1.908	1.489	2.45	97.55

Since these results indicate a marked decomposition of the sugars under rather extreme conditions, the question naturally arose as to what sugars were the most susceptible to variations of conditions. Neuman<sup>4</sup> studied the decomposition of glucose by dilute acid at different temperatures and concluded that 175° C. marked the "critical point" beyond which it is useless to investigate the production of sugars. Since mannose constitutes a considerable proportion of the sugars that result from the hydrolysis of softwoods, it was desirable to repeat this series of experiments upon this sugar. The results obtained are given in Table VI and Fig. II. In the case of mannose 1.25 per cent sulfuric acid was used as compared with 1.0 per cent and 1.5 per cent in Neuman's work. The decomposition of mannose under similar conditions is apparently the same as that of glucose, since the curve showing the rate of decomposition parallels those of glucose.



<sup>4</sup> Dissertation, Dresden, 1910, p. 31.

## Report of Committee on Fertilizer Legislation

A report of the Committee on Fertilizer Legislation of the Division of Fertilizer Chemistry of the AMERICAN CHEMICAL SOCIETY was presented at the Milwaukee meeting by J. E. Breckenridge. This report consisted of a review of the fertilizer legislation of importance enacted during the past year, referring particularly to the new Florida law relating to the guarantee of available and soluble nitrogen, and to the new North Carolina law pertaining to the showing of the mineral and organic nitrogen on the source tags.

# Partial Hydrolysis of White Spruce Cellulose<sup>1</sup>

## Preliminary Note

By E. C. Sherrard and G. W. Blanco

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**D**URING the investigation of the hydrolysis of spruce cellulose, attention was directed to the presence of considerable quantities of easily hydrolyzable material contained in cellulose prepared by the Cross and Bevan method. That this material is not present as such but is produced by mild hydrolysis is indicated by the fact that, although after isolation it is extremely soluble in water, it can be removed from the cellulose only upon prolonged boiling with water. It has been obtained in the form of a white powder by concentrating the water extract to a thick sirup and precipitating with ethyl alcohol. This powder has a relatively small reducing value and gives no test for mannose. After hydrolysis with dilute acids, however, the reducing value is increased to about five times that of the original and a sharp test for mannose is obtained. Pentoses are also present in considerable quantity.

This solid material has been partially purified by dissolving in water and fractionally precipitating with alcohol. The product so obtained is so extremely soluble in water that when exposed to moist air the particles or crystals coalesce and finally liquefy. Some doubt exists at this time as to the nature of the material, since on two occasions well-formed, needle-like crystals were present when examined under a low power microscope in the presence of the mother liquor. While under examination these needles would absorb water and completely dissolve. Subsequent attempts to purify further by repeated reprecipitations resulted in obtaining the material in an extremely fine powder. Upon long standing, needles again appeared but they constituted only about one-half of the total powder, the remainder consisting of the fine transparent particles noted above. The fine material showed the same tendency to dissolve when exposed to air or moisture.

The presence of this water-soluble material in the cellulose

<sup>1</sup> Presented before the Division of Cellulose Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

lose was at first ascribed to a mild hydrolysis by residual acetic acid during drying. As a consequence, a new quantity of cellulose was prepared and hydrolyzed immediately after the final chlorination both before and after drying. A second portion was treated with acetic acid in the usual way and then hydrolyzed before and after drying. A third sample had the acetic acid removed by washing with dilute ammonium hydroxide and drying. The results of these experiments are given in Table I. It will be noticed that drying has the most pronounced effect in increasing the water-soluble material as indicated by the loss in weight of the cellulose. Treatment with acetic acid without subsequent drying decreases the water-soluble, but after drying an increase is obtained. The removal of acetic acid by ammonia decreases the yield quite markedly. The reducing values given in terms of dextrose agree quite well with the quantity of cellulose lost upon hydrolysis, except that after acetic acid treatment the reducing value of the water-soluble material is increased. Successive refluxing indicated that not all the material is removed until after the third 4-hour treatment with boiling water. The ratio of reducing values of the water-soluble material before and after hydrolysis with dilute sulfuric acid varies from 1:2 to 1:5, and indicates that partial hydrolysis occurred during extraction or that the material is not homogeneous. The ratio of mannose to total reducing material is fairly constant in Experiments 1 and 5, but Experiment 2 indicates that hydrolysis is more complete after drying, while 6B indicates additional hydrolysis by the combined action of acetic acid and heat.

Two samples of the water-soluble material were prepared in the form of a white powder and were subjected to an examination, the results of which are given in Table II. The reducing values are given in terms of dextrose. Sample 1 was prepared in the usual way, while in Sample 2 the cellulose was washed with about 20 liters of boiling water to make sure that no water-soluble material remained in the cellulose.

TABLE I—EXPERIMENTS ON THE REFLUXING OF WHITE SPRUCE CROSS AND BEVAN CELLULOSE WITH WATER FOR 4 HOURS

Expt.	Condition of Cellulose	TREATMENT	EXAMINATION OF WATER EXTRACT									
			Cellulose Extracted Per cent of Original	Total Cellulose Extracted Per cent of Original	Per cent of Reducing Material	Reducing in Per cent of Cellulose Removed	Total Reducing Material Per cent of Total Cellulose Removed	Per cent of Reducing Material	Reducing Material in Per cent of Cellulose Removed	Reducing Material in Per cent of Total Cellulose Removed	Mannose Per cent of Original Cellulose	Mannose Per cent of Total Reducing Material
1	Wet	First refluxing with water. Before acetic acid treatment.	13.95	13.95	1.00	7.17	...	5.00	35.84	...	1.17	23.40
3	Dry	Refluxing of residue from Expt. 1.	7.62	21.57	0.62	8.14	7.51	3.13	41.07	37.70	...	...
4	Dry	Refluxing of residue from Expt. 3.	1.28	22.85	...	...	...	...	...	...	...	...
2	Dry	First refluxing with water. Before acetic acid treatment.	21.80	21.80	3.01	13.80	13.80	8.21	37.64	...	3.80	46.16
5	Dry	Refluxing of residue from Expt. 2.	5.87	27.61	1.28	21.80	15.50	4.51	77.00	46.00	1.26	28.00
6A	Wet	First refluxing after acetic acid treatment	6.80	6.80	3.15	46.32	...	6.60	97.25	...	2.13	32.30
7	Dry	Cellulose after acetic acid treatment, washed with 1 per cent NH <sub>4</sub> OH and refluxed with water.	4.08	4.08	0.34	8.33	8.33	2.30	56.37	...	...	...
6B	Dry	First refluxing after acetic acid treatment.	16.24	16.24	3.96	24.38	...	7.49	46.12	...	4.97	66.30
9	Dry	Residue from Expt. 6B	4.72	20.96	0.93	17.58	23.40	3.25	...	...	...	...
10	Dry	Residue from Expt. 7	1.54	6.62	Trace	...	...	1.15	74.67	52.11	...	...
11	Dry	Residue from Expt. 6A	7.15	13.95	1.00	14.00	29.03	3.28	45.87	70.83	...	...
12	Dry	Hydrolysis of cellulose residue from Expt. 9 with 5% HCl.	21.72	42.68	...	...	...	14.88(HCl)	68.51	60.03	3.20	...

TABLE II—REFLUXING OF CROSS AND BEVAN CELLULOSE-WATER EXAMINATION OF PRECIPITATED MATERIAL

DETERMINATION	Sample 1 Per cent	Sample 2 Per cent
Cellulose removed.....	16.56	11.00
Precipitated material.....	12.57	12.03
Reducing material before hydrolysis.....	15.96	11.20
Reducing material after hydrolysis, 4.5% H <sub>2</sub> SO <sub>4</sub> .....	70.73	57.21
Mannose in per cent of sample.....	33.37	27.00
Mannose in per cent of total reducing material.....	47.18	47.00
Pentose in per cent of sample.....	19.30	21.58
Pentose in per cent of total reducing material.....	27.28	37.70

The yield of 12 per cent water-soluble material corresponds approximately with the loss in the preparation of  $\alpha$ -cellulose and is a trifle less than the loss in cellulose. The material upon ignition leaves no ash, is insoluble in alcohol,

chloroform, acetone, methanol, and benzene. The melting point is not definite but the material begins to darken at 220° C.; at 235° C. it turns dark and begins to decompose. It shows no reaction with phenylhydrazine. The quantity of pentose contained corresponds to 37.4 per cent of the pentose present in the original cellulose. The mannose content of the powder corresponds to 42.8 per cent of that contained in the original cellulose.

No attempt is made at this time to ascribe a definite chemical constitution to this material. Were it not for its apparently crystalline form, it might well be considered a mannan. Further investigation of this material is now under way.

## The Estimation of Pentoses and Pentosans<sup>1,2</sup>

### I—The Formation and Distillation of Furfural

By Norville C. Pervier and Ross A. Gortner

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THAT the wide distribution of the pentosans in nature, as pointed out by Tollens in 1891, may be of considerable significance in plant economy, is indicated by the work of Spoehr, Hooker, and Rosa. These substances also constitute a large portion of the nitrogen-free extract of many animal feeds and have been the subject of numerous experiments in animal metabolism. (McCullum and Brannon, Swartz.) The pentosan determination has also been used as a basis for determining the degree of milling of flours (Gerum). It is apparent, then, that a convenient and accurate method for estimating these substances is very necessary. Because of the serious shortcomings inherent in the official method for determining pentosans, the present work was undertaken.

#### HISTORICAL

FORMATION OF FURFURAL—Döbereiner (1832) first obtained furfural by the distillation of sugar with pyrolusite and sulfuric acid. Stenhouse (1840) later showed the pyrolusite to be unnecessary, while Völckel (1853) found that furfural was a decomposition product of many carbohydrate materials. Stenhouse (1850) was the first to prepare furfural on any appreciable scale. He distilled wheat bran with strong sulfuric acid. The use of a strong solution of zinc chloride in the distillation procedure was proposed by Babo (1853). Stone and Tollens (1888) and Wheeler and Tollens (1889) used sulfuric acid of various concentrations. Phosphoric acid was tried by Mann, Krüger, and Tollens (1896). Glacial acetic acid was used by Testoni (1917). It was early recognized, however, that the use of 12 per cent hydrochloric acid gave better yields of furfural, in a shorter time, with more accurate duplication of results, and with less "humin" formation, than when any other acid was used [Allen and Tollens (1890), Günther and Tollens (1890), de Chalmot and Tollens (1891), Counciler (1892), Stone (1897), Hauers and Tollens (1903), Jolles (1905), Ling and Nanji (1921)]. Moreover, even acid of 12 per cent concentration has an appreciable de-

Following a review of previous work on the formation of furfural, Part I is a study of the factors influencing the production of furfural from pure arabinose, pure xylose, gum arabic, and pine sawdust. A method for distilling pentoses from acid solution by steam is described, in which theoretical yields of furfural are discussed.

Part II, which will appear in a subsequent issue, describes several new volumetric methods for the determination of furfural in aqueous solution, and includes a bibliography on pentoses and pentosans.

structive effect on furfural, as shown by Fraps (1901), Jolles (1905), Mayer and Tollens (1907), and van Haarst and Olivier (1914), and also upon pentose as argued by Unger and Jäger (1903), and Fraps (1915). Also, araban and fucosan, as well as the corresponding sugars, produce furfural very slowly so that the yield from them is lower than that from others

of the group due to the destructive action of the acid, as has been shown by the above-mentioned writers and by Kunz (1916). The yields of furfural usually obtained are recorded in Table I.

TABLE I—YIELDS OF FURFURAL OBTAINED FROM PENTOSE SUGARS BY DISTILLATION WITH ACIDS

Pentose Recovery Per cent	Yield of Furfural Per cent	OBSERVER
	Arabinose	
75.00	48.00	Browne (1912)
74.32	47.56	Unger and Jäger (1903)
74.54 to 82.35	47.7 to 52.7	DeChalmot and Tollens (1891)
73.44	47.00	MacKenzie (1913)
100	64.00	Ling and Nanji (1921)
98.7 to 100.8	64.00	Jolles (1905)
	Xylose	
89.85	57.50	Unger and Jäger (1903)
90.00	57.60	Browne (1912)
87.5 to 92.2	56 to 59	DeChalmot and Tollens (1891)
97.5 to 100.3	64.00	Jolles (1905)

Substances other than pentose may also yield furfural on distillation with acid. Glucuronic acid is one of these, and Tollens (1909) has determined it by a method identical with that for pentoses. However, glucuronic acid is rarely encountered. It has also been claimed that oxycellulose produces furfural. This statement appears to be based on the early work of Cross, Bevan, and Beadle (1894), Vignon (1899), and Faber and Tollens (1899), which was done before the production of hydroxymethylfurfural from hexose materials was established. Moreover, much of the furfural said to be produced from cellulose may really have its origin in true pentosans (hemi- and ortho-pentosans) contained in the cellulose. [König and Rump (1914), Schwalbe (1918), Heuser and Haug (1918), Schwalbe and Becker (1920).] Other interfering substances have been mentioned, but little is known concerning their composition and distribution. Bray and Staidl (1922) claim to have worked out a correction to lessen the error due to these substances, but have not published it.

TESTS FOR FURFURAL—For determining when distillation is complete, aniline acetate has usually been used. This is prepared by adding glacial acetic acid to a mixture of equal parts of colorless aniline and water until the mixture suddenly clears. It has been frequently observed, however, that acetic acid often gives a positive test, due to the presence in it of furfural, as was shown by V. Meyer (1878). To avoid the difficulty, the use of

<sup>1</sup> Presented before the Division of Biological Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Received April 10, 1923.

<sup>2</sup> Published with the approval of the director as Paper No. 382, Journal Series Minnesota Agricultural Experiment Station. Condensed from a thesis submitted by Norville C. Pervier to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of doctor of philosophy.

concentrated hydrochloric acid has been recommended by Tolman and Trescott (1906), Cunningham and Doree (1914), and Schorger (1917); but strong mineral acids may destroy the color, as has been argued by de Chalmot (1893) and by Baker and Hulton (1916). Hydroxymethylfurfural, arising from hexoses during acid distillation, does not interfere, since it is formed so slowly and in such small quantities [van Ekenstein and Blanksma (1910), Cunningham and Doree (1914)]. Jolles (1905) believed the aniline test was not sufficiently sensitive, and used Bial's orcinol-ferric chloride test solution. Van Haarst and Olivier (1914) preferred phloroglucinol. The present official method for the determination of pentoses makes no mention of the use of an indicator. Distillation is simply carried out at a definite rate until a definite volume of distillate has been received.

#### OFFICIAL METHOD AND SUGGESTED MODIFICATIONS

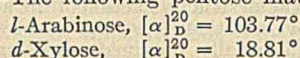
The official method of distillation is to heat the sample with 12 per cent hydrochloric acid at such a rate that 30 cc. pass over in 10 minutes. Thirty cubic centimeters more of 12 per cent acid are then added and the process is repeated until 360 cc. of distillate have been collected.

The following modifications have been proposed:

Cross, Bevan, and Smith (1895) suggested the use of the constant level apparatus of Chorley (1895), and Stanek (1900) devised an automatic apparatus to facilitate the procedure, but these have not come into use. Heuser (1921) found that higher and more accurate yields of furfural were obtained if the weighed sample of pentosan was dissolved in normal sodium hydroxide solution before distilling with acid. Dekker (1914) added 500 cc. of 12 per cent hydrochloric acid and distilled directly. His results were low. Grund (1902) added and distilled in 50-cc. fractions and recorded a more intensive action by the change. Jolles (1905) added the acid, and steam-distilled the hydrolysate, heating the latter so that its volume decreased to about half while 800 cc. of water were distilled through it. More acid was then added and the process repeated until no more furfural was produced. Jolles claimed to get theoretical conversions of pentoses (arabinose and xylose) to furfural, the only such claim made in the literature.

#### EXPERIMENTAL

**MATERIALS**—The following pentose materials were used:



As pentosan-containing materials, pine sawdust and gum arabic were used, each being ground to 50 mesh. These materials were distilled with acid according to the procedures outlined below and the furfural-containing distillate was titrated by the method proposed in Part II, which is briefly as follows:

**Method of Determining Furfural**—A small aliquot of the distillate was titrated with standard alkali to determine its acidity. This aliquot was then re-added to the distillate and sufficient hydrochloric acid or strong sodium hydroxide solution also added to give a final acidity of about 4 per cent. Ten cubic centimeters of 20 per cent potassium bromide were then added and the resulting solution was titrated with standard potassium bromate solution in the manner described in Part II.

**INDICATOR**—For deciding when distillation was complete, strips of filter paper were used which had been dipped in aniline hydrochloride solution and dried. The aniline hydrochloride solution was freshly prepared from colorless aniline and C. P. hydrochloric acid.

**EFFECT OF ACIDITY DURING DISTILLATION**—Owing to the ease with which furfural is destroyed by strong acid, a study of the acidities obtained during distillation was regarded essential. Two 12 per cent hydrochloric acid distillation procedures were studied—(1) the method of the Association of Official Agricultural Chemists (1920), which has been said to yield low furfural figures; and (2) the method of Jolles, in which theoretical yields were claimed. In both studies the boiling point temperatures were taken as an index to the concentration of acid present in the distillation flasks.

**OFFICIAL DISTILLATION PROCEDURE**—The samples were distilled as directed in the official method until 360 cc. had

distilled over. In each instance the distillation began at 103° to 104° C., but had reached 108.55° C. (corrected) by the time 60 cc. had been distilled out. Subsequent additions of 12 per cent hydrochloric acid caused a temporary drop of 0.6° C., but the constant boiling temperature was very soon again reached. The greater part of the distillation took place, therefore, from acid of 18 to 20 per cent concentration. The data are recorded in Table II. The furfural in the distillate was determined by the titrimetric method described in Part II of this paper.

TABLE II—PENTOSE DETERMINATIONS. DISTILLATIONS BY THE OFFICIAL METHOD  
(Volume of distillate, 360 cc.)

Weight of Sample Gram	0.1 N KBrO <sub>3</sub> Cc.	Pentose Found (Factor = 0.007505)		Recovery Per cent	
		Gram			
<i>Arabinose</i>					
0.2016	25.50	0.1914		94.9	
0.2005	25.75	0.1943		96.8	
0.2020	25.35	0.1903		94.2	
0.2045	26.00	0.1951		95.4	
				AVERAGE	95.3
<i>Xylose</i>					
0.2038	26.00	0.1951		95.7	
0.2022	25.75	0.1943		96.1	
0.2016	25.80	0.1936		96.0	
0.2009	25.75	0.1943		96.7	
				AVERAGE	96.1

It will be noted that a recovery of 95.3 per cent from arabinose and 96.1 per cent from xylose was secured. These values are higher than have been found by most workers with the exception of Jolles (1905), and (possibly) Ling and Nanji (1921). Both Jolles and Ling and Naji, as well as the writers, used titrimetric methods for determining the furfural. If the higher results which the writers obtained are not due to a more accurate method of determining the furfural in the distillate, they are at a loss to explain their high values, especially those of arabinose.

TABLE III—PENTOSE DETERMINATIONS. DISTILLATIONS BY STEAM FROM 12 AND 20 PER CENT HYDROCHLORIC ACID SOLUTIONS

Per cent Acid	Weight of Sample Gram	Volume of Distillate Cc.	0.1 N KBrO <sub>3</sub> Cc.	Pentose Found (Factor = 0.007505)		Recovery Per cent
				Gram		
<i>Arabinose</i>						
12	0.2030	715	27.00	0.2026		99.8
	0.2020	650	27.00	0.2026		100.3
	0.2014	900	26.80	0.2011		99.9
	0.2005	1200	26.70	0.2004		99.9
20	0.2030	1250	26.75	0.2008		100.2
	0.2040	755	26.75	0.2008		100.2
	0.2000	900	26.75	0.2008		100.3
	0.2010	1050	26.75	0.2008		99.9
				AVERAGE		100.1
<i>Xylose</i>						
12	0.2003	400	26.65	0.2000		99.8
	0.2010	620	26.75	0.2008		99.9
	0.2040	1000	27.00	0.2026		99.3
	0.2020	425	26.85	0.2015		99.7
20	0.2035	300	27.25	0.2045		100.4
	0.2045	375	27.25	0.2045		100.0
	0.2033	500	27.15	0.2038		100.2
	0.2016	825	26.80	0.2011		99.8
				AVERAGE		99.9

**DISTILLATION METHOD OF JOLLES**—Jolles advised that the pentose sample be placed in a distilling flask with 200 cc. of 12 per cent hydrochloric acid and steam-distilled, boosting at such a rate that the volume decreased to about 100 cc. while the steam from 800 cc. of water was led through it. More 12 per cent hydrochloric acid was then added, and the process repeated as long as furfural was produced. The temperatures obtained during this type of distillation were always from 103° to 104° C., which indicated that the acidity of the hydrolysate remained in the neighborhood of 12 per cent throughout the distillation. The lack of destruction of furfural observed by Jolles must then be due either to the low acidity during distillation, or to the prompt removal of the furfural by the current of steam passing through, or both.

To determine which of these factors was the more important, samples of pure pentoses and of the pentosan mate-

rials mentioned above were distilled with steam from both 12 and 20 per cent hydrochloric acid. The heat was adjusted so that temperatures of 103° to 104° C. were maintained in the 12 per cent distillation, while temperatures of 107° to 108° C. were held in the 20 per cent distillations. Within the limits of experimental error, theoretical results were in all cases obtained from the pentoses used, regardless of the concentration of acid. This is shown in Table III. The pentosan materials gave constant yields, indicating that no loss of furfural had occurred. (Table IV) Furthermore, the rate of distillation did not affect the yield, as shown by the marked differences in volumes of distillates obtained. Evidently, even a slow current of steam is sufficient to sweep out the furfural as fast as it is formed from the pentoses.

TABLE IV—PENTOSAN DETERMINATIONS. DISTILLATIONS BY STEAM FROM 12 AND 20 PER CENT HCl SOLUTIONS

Per cent Acid	Weight of Sample Grams	Volume of Distillate Cc.	0.1 N KBrO <sub>3</sub> Cc.	Pentosan Found (Factor = 0.006605) Gram	Pentosan Per cent
<i>Gum Arabic</i>					
12	0.5018	820	24.50	0.1618	32.2
	0.5033	1160	24.25	0.1602	31.8
	0.5053	725	24.65	0.1628	32.2
	0.5016	925	24.40	0.1611	32.1
20	0.5004	640	24.25	0.1602	32.0
	0.5053	685	24.50	0.1618	32.0
	0.5047	940	24.50	0.1618	32.1
	0.5036	900	24.50	0.1618	32.1
AVERAGE					
<i>Sawdust</i>					
12	1.0020	935	23.25	0.1535	15.3
	1.0017	875	23.25	0.1535	15.3
	1.0056	1000	23.35	0.1542	15.3
	1.0064	900	23.50	0.1552	15.4
20	2.0020	615	46.40	0.3064	15.3
	2.0014	710	46.25	0.3054	15.3
	2.0049	625	46.50	0.3071	15.3 <sup>a</sup>
	2.0032	600	46.50	0.3071	15.3 <sup>a</sup>
12	1.0026	575	23.00	0.1519	15.1 <sup>a</sup>
	1.0077	870	23.25	0.1535	15.2 <sup>a</sup>
	1.0018	530	23.25	0.1535	15.3 <sup>a</sup>
AVERAGE					
15.3					

<sup>a</sup> These distillations were carried out according to Heuser's method (1921), the samples being macerated with 4 per cent sodium hydroxide before distilled with acid. No increased yield of pentosan was obtained. Heuser's determinations always ran 4 per cent higher by this treatment. Hence the foregoing data further substantiate the claim that theoretical yields of furfural are obtained from pentosans by the proposed distillation procedure.

A comparison of the pentose results in Tables II and III indicates that the reason low results are obtained by the official method is that some of the furfural is destroyed by long contact with strong acid. Moreover, this destructive effect can be entirely eliminated by carrying a slow current of steam through the hydrolysate, thereby removing the furfural as fast as it is produced. Hence the following method for the quantitative production of furfural from pentose materials is proposed.

**PROPOSED METHOD FOR DISTILLATION OF PENTOSSES—**Place a weighed (0.20 to 5.0 grams depending upon the pentose or pentosan content) sample of the material, and 200 cc. of 12 per cent hydrochloric acid (specific gravity, 1.06) in a 750-cc. distilling flask fitted up for steam distillation. Conduct a slow current of steam into the mixture and as soon as the mixture reaches the boiling temperature heat the distilling flask with a low flame so that the boiling temperature remains between 103° to 105° C. as measured by a thermometer inserted in the vapor in the neck of the distilling flask. By observing this precaution the addition of fresh acid will rarely be required. About one-half of the original volume of liquid should remain in the flask at the end of the distillation. Continue distillation until a drop of the distillate no longer gives a red coloration with aniline test paper on being allowed to stand 3 to 5 minutes.

By following this procedure theoretical yields of furfural have been obtained from all the pure pentose materials which have been tested. Representative data are found in Table V.

TABLE V—PENTOSE DISTILLATIONS BY THE PROPOSED METHOD

Weight of Sample Gram	0.1 N KBrO <sub>3</sub> Cc.	Factor = Grams Pentose Cc. 0.1 N KBrO <sub>3</sub>
<i>Arabinose</i>		
0.2000	26.50	0.00755
0.2005	26.50	0.00755
0.2015	26.75	0.00753
0.2021	26.85	0.00752
0.2030	27.00	0.00752
0.2025	27.00	0.00750
0.2037	27.25	0.00747
0.2040	27.25	0.00748
AVERAGE		
0.007515		
<i>Xylose</i>		
0.3020	40.00	0.00755
0.3035	40.30	0.00753
0.3010	40.00	0.00752
0.3027	40.30	0.00751
0.3040	40.45	0.00754
0.3070	41.00	0.00749
0.3082	41.20	0.00749
0.3044	40.50	0.00752
AVERAGE		
0.007510		
TOTAL AVERAGE		
0.007517		
THEORETICAL		
0.007505		

## CONCLUSIONS

The data presented seem to warrant the following conclusions:

1—Distillations of pentose materials, carried out according to the method of the Association of Official Agricultural Chemists, take place from hydrochloric acid of 18 to 20 per cent concentration, instead of from 12 per cent acid as usually stated.

2—Hydrochloric acid of this concentration has a considerable destructive effect on furfural, and is no doubt partly responsible for the low yields of furfural that are obtained from all pentoses when the official method is used.

3—The passage of a slow current of steam through the distillation mixture is sufficient to carry the furfural off as rapidly as it is formed, thereby avoiding the destruction of furfural by long contact with strong acid.

## Motion Pictures to Show Cotton Dusting Method

Two thousand feet of "movie film" were recently made by the motion picture office of the Department of Agriculture, showing the method of spreading calcium arsenate dust over fields of cotton by airplane for control of the boll weevil. The pictures were taken at Tallulah, La., where the experiments in cotton dusting by airplane are being conducted under the direction of B. R. Coad, in charge of the Delta Laboratory there.

Results obtained by this method of spreading the poison have been sufficiently satisfactory to give promise of the use of airplanes on a commercial scale in fighting the boll weevil, and the film was made largely for the purpose of creating an interest in further development of detail and to show the progress already made. It will be shown first before officials of the Department of Agriculture and of the War Department, which is cooperating in the tests by supplying the air machinery and personnel.

The best results to be obtained in spreading the poison in this manner are to be had by early morning flights when the air is still and there are no air pockets to make flying more dangerous. Three days were taken to complete the making of this negative and ten flights of from 10 to 30 minutes each were made. The planes used were two De Haviland bombers which have a speed of from 90 to 100 miles an hour.

## McBain Tells Boston Chemists about Soap

A number of chemists of the Northeastern Section met James W. McBain of the University of Bristol, England, at luncheon on Monday, October 15. With J. F. Norris of the Massachusetts Institute of Technology as toastmaster, greetings were tendered the guests by A. B. Lamb of Harvard, H. P. Talbot of the Massachusetts Institute of Technology, L. C. Newell of Boston University, and L. C. Pratt of the Merrimac Chemical Company. In the evening Professor McBain addressed the regular monthly meeting of the Northeastern Section on "A Study of Soap Solutions and Its Bearing on Colloid Chemistry." Supported by many fine microphotographs, the speaker argued convincingly that a soap gel has a filamentary or "brush-heap" structure.

# Charts for Estimating Temperature Distributions in Heating or Cooling Solid Shapes<sup>1</sup>

By H. P. Gurney and J. Lurie

BOSTON BELTING CO., BOSTON, MASS.

IN many technical processes large solid shapes are subjected to temperature changes in order to attain certain physical or chemical results. In so doing the temperature-time relations, irrespective of what point may be taken as the time origin, may differ considerably and in consequence cause to exist different degrees of physical inhomogeneity. Technical examples that may be cited are found to abound in rubber, steel, glass, and other industries.

The temperature-time relations in the interior of solid bodies which are either being heated or cooled may be empirically determined by inserted thermometers, thermocouples, or other temperature-measuring apparatus, or may be calculated from the assumed conditions, in conjunction with the physical constants of the materials, the surrounding contours, shapes, and media. The fact that thermal physical data are not so complete as they might be, or that technical conditions can rarely be made to coincide with the theoretical prototypes, does not negative the value of such estimations, but does require that the precision of the computed results should not be overestimated. Where empirical observations and theoretical calculations may be made concurrently, new physical constants may be determined which will be found to be more reliable in predicting other time-temperature relations under different, though similar conditions.

The curves in Figs. 1, 2, 3, 4, and 5 were obtained by converting some of the more common formulas for heat diffusion into expressions containing pure ratios or nondimensional variables only, thereby enormously reducing the necessary basic calculations as well as extending the field of applicability.

<sup>1</sup> Received May 25, 1923.

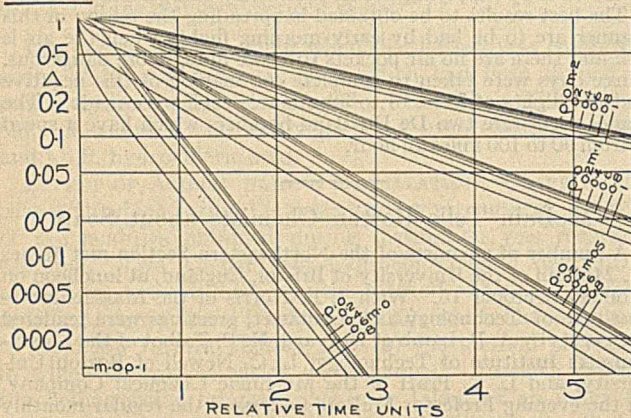


FIG. 1—UNACCOMPLISHED TEMPERATURE-CHANGE RATIOS OF A SLAB INITIALLY AT UNIFORM TEMPERATURE AND APPROACHING ANOTHER UNIFORM TEMPERATURE.  $\rho$  DEFINES RELATIVE DISTANCE FROM MIDPLANE;  $m$  DEFINES RELATIVE SURFACE RESISTIVITY

*This paper is abstracted from a more complete exposition entitled "On the Heating and Cooling of Certain Solid Shapes," a special paper by one of the writers deposited in the library of the Massachusetts Institute of Technology through the courtesy of the Chemical Engineering Department. In the original it has not been possible to go exhaustively into the effect of time-temperature relations upon the physical properties of the materials mentioned. Some of these relations are fairly well understood. A better knowledge of time-temperature relations in such processes as the vulcanizing of rubber, the hardening of steel, or the annealing of glass in conjunction with graphical application of the formulas of heat diffusion may help to realize Fourier's wish expressed in the introduction of the memoir, "Theorie du mouvement de la chaleur dans les corps solides (1812)," that his mathematics be applied to industry.*

In Figs. 1 to 5, the abscissas 0 to 5.5 are in units obtained by multiplying time,  $t$ , into the thermal diffusivity,  $h^2$ , of the material, and then dividing this product by the square of some linear dimension of the shape in question, such as the radius of the sphere or cylinder, or by one-half the thickness of the slab,  $R^2$ . The expression generally employed in denoting this relation is  $\tau = th^2/R^2$ , where the symbols employed are

in the order mentioned.

The ordinates 1 to 0.002 refer to the ratios of unaccomplished temperature change to the total, limiting, or maximum possible temperature change that the thermal environment can impress upon any part of the body—that is, the temperature at the start is conceived to be unit and to approach or eventually become zero. At any time,  $t$ , in question the temperature is conceived to differ from the final temperature by a temperature ratio,  $\Delta$ , which approaches zero as a limit. The ordinates are functions of two other variables besides time. The first variable,  $\rho$ , is the ratio of the distance from the center, axis, or midplane to the point in question to the distance from the surface to the axis, center, or midplane. This ratio,  $\rho$ , is therefore zero at the center, axis, or midplane, and unit at the surface, with intermediate values at points between. In Fig. 5, dealing with the semi-infinite solid, only the point in question is considered; hence,  $\rho$  is not involved.

The other function,  $m$ , is the ratio of the thermal conductivity,  $k$ , of the material to the product of the thermal surface conductivity,  $E$ , into the radius,  $R$ , or semithickness of the shape. This is expressed symbolically by  $m = k/ER$ . If the surface emissivity is infinity,  $E = \infty$ . That is, if the surface of the body instantly assumes the temperature of

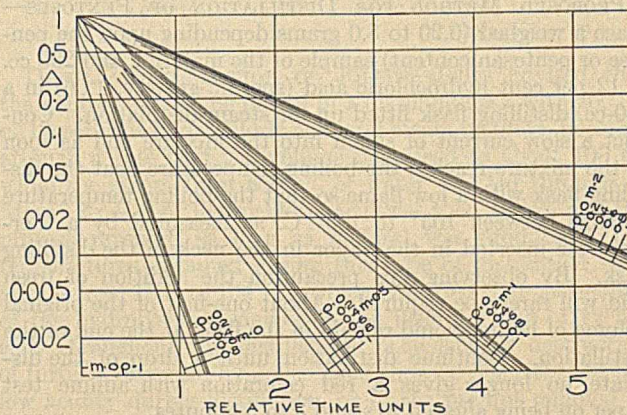


FIG. 2—UNACCOMPLISHED TEMPERATURE-CHANGE RATIOS OF A CYLINDER INITIALLY AT UNIFORM TEMPERATURE AND APPROACHING ANOTHER UNIFORM TEMPERATURE.  $\rho$  DEFINES RELATIVE DISTANCE FROM AXIS;  $m$  DEFINES RELATIVE SURFACE RESISTIVITY

the surrounding media, then  $m = \text{zero}$ . If the surface is perfectly insulated ( $E = 0$ ), then  $m = \infty$ .  $m$  may also be expressed as the ratio of surface thermal resistivity to the radius multiplied into the resistivity of the solid material. This follows because of the fact that these are reciprocals, respectively, of  $E$  and  $k$ .

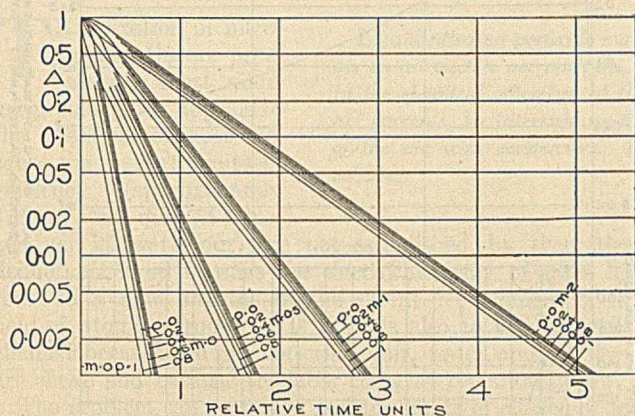


FIG. 3—UNACCOMPLISHED TEMPERATURE-CHANGE RATIOS OF A SPHERE INITIALLY AT UNIFORM TEMPERATURE AND APPROACHING ANOTHER UNIFORM TEMPERATURE.  $\rho$  DEFINES RELATIVE DISTANCE FROM CENTER;  $m$  DEFINES RELATIVE SURFACE RESISTIVITY

Figs. 1, 2, and 3 exhibit values of  $\Delta$  (between 1 and 0.001) from  $\tau = 0$  to  $\tau = 5.5$ , for  $\rho = 0, 0.2, 0.4, 0.6, 0.8$ , and  $1.0$ , and  $m = 0, 0.5, 1$ , and  $2$ . For constant values of  $\Delta$ ,  $\tau$  is nearly linearly proportional to  $m$ ; hence, interpolations up to 2 are quite safe, and since the proportionality is even closer the greater  $m$  is, extrapolation may be carried up to  $m = 10$  without a greater error than usually resides in the assumed physical constants.

Fig. 4 exhibits the values of  $\Delta$  for  $\rho = 0, 0.2, 0.4, 0.6, 0.8$ , in a slab, cylinder, or sphere, where the surface is subjected to uniform change in temperature, the total temperature change at any time,  $t$ , being considered unity.

Fig. 5 was prepared to take care of a special case of either Figs. 1, 2, or 3. This figure shows not only the relative temperatures  $\Delta$  for  $m = 0, 0.5, 1$ , and  $2$ , but its differential,  $d\Delta/d\tau$ , with respect to  $\tau$  for points relatively near the surface of any type of solid body—that is, where  $\rho$  lies between 0.9 and 1.0. For lower values of  $\rho$  there would be an increasing error. In this figure  $\tau = th^2/R^2$  is replaced by  $\tau = th^2/X^2$ , where  $X$  is the linear distance from the point in question to the surface.

To illustrate and apply these figures more definitely, three examples will be adduced, and the transformation from arithlog to arithmetic ordinates will be made.

A slab of rubber 2.5 inches in thickness (hence 3.17 centimeters from surface to midplane) is at a temperature of  $80^\circ\text{F}$ . uniformly distributed, and is placed suddenly in surroundings (such as a heated press) maintained at a constant temperature of  $280^\circ\text{F}$ ., and the body is allowed to heat up. It is desired to ascertain the temperature-time relations at the midplane (where  $\rho = 0$ ) and at a point 0.25 inch from the surface (where  $\rho = 0.8$ ). The thermal conductivity,  $K$ , of the rubber is 0.0004 calorie per centimeter cube per second, while the surface emissivity,  $E$ , is 0.0005, and the thermal diffusivity,  $h^2$ , is 0.00087 sq. cm. per second. Under these conditions

$$m = \frac{k}{ER} = \frac{0.0004}{0.0005 \times 3.17} = 0.25$$

and at  $\tau = 1$ ,  $t$  must equal 11,600 seconds, or 3.22 hours, in order that the following condition be satisfied:

$$1 = \frac{th^2}{R^2} = \frac{t \times 0.00087}{3.17 \times 3.17}$$

The relation between temperature Fahrenheit,  $\Theta$ , and  $\Delta$  may be graphically determined by connecting points  $\Delta = 1$ ,  $\Theta = 80^\circ\text{F}$ ., and  $\Delta = 0$ ,  $\Theta = 280^\circ\text{F}$ ., by a straight line or by relation

$$\Theta = 280 - \Delta(280 - 80)$$

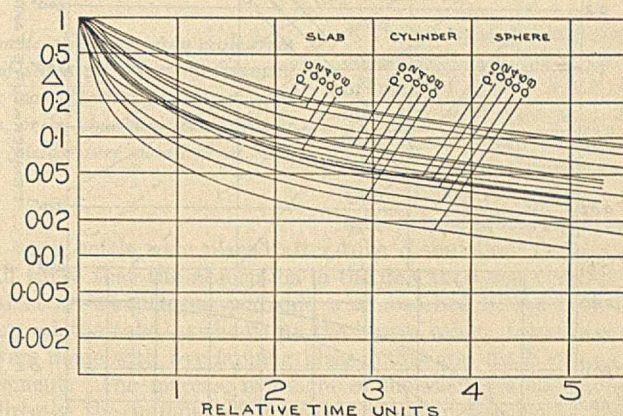


FIG. 4—UNACCOMPLISHED TEMPERATURE-CHANGE RATIOS AT POINTS IN A SLAB CYLINDER OR SPHERE INITIALLY AT UNIFORM TEMPERATURE BUT WITH SURFACE TEMPERATURE UNIFORMLY VARYING FROM INITIAL VALUE

In Fig. 6, upper part, Fig. 1 is duplicated for  $\rho = 0$  and  $\rho = 0.8$ , and  $m = 0$  and  $0.5$ . New dotted lines for  $m = 0.25$  are drawn between  $m = 0$  and  $m = 0.5$ , interpolating proportionally between intersections of these lines and lines of constant  $\Delta$ . At the right the ordinates are renumbered in terms of temperature Fahrenheit. In Fig. 6, lower part, these dotted lines are converted into solid lines on arithmetic ordinates.

A large ingot of steel is suddenly cooled at its surface from  $1100^\circ$  to  $100^\circ\text{F}$ ., hence undergoing a drop in temperature of  $1000^\circ\text{F}$ . It is desired to ascertain the time-temperature rate of change relations at a distance of 1 cm. from the surface, assuming the thermal diffusivity of steel to be 0.15 sq. cm. per second.

At  $\tau = 1$ , expression  $\tau = th^2/X^2$  is satisfied if  $t = 6.35$  seconds, and in place of  $d\Delta/d\tau$ ,  $d\Theta/dt$ ,  $1000^\circ\text{F}$ . per 6.35 seconds or  $157.5^\circ\text{F}$ . per second. In Fig. 7, upper part, the ordinates are correspondingly renumbered, while in Fig. 7, lower part, the relations are converted over and expressed on arithmetic ordinates.

A slab of glass 1.5 inches thick (hence 1.9 centimeters from surface to midplane) is subjected to a uniform temperature rate of increase of  $1^\circ\text{C}$ . per minute starting at  $20^\circ\text{C}$ . and proceeding uniformly for 30 minutes so that the surface

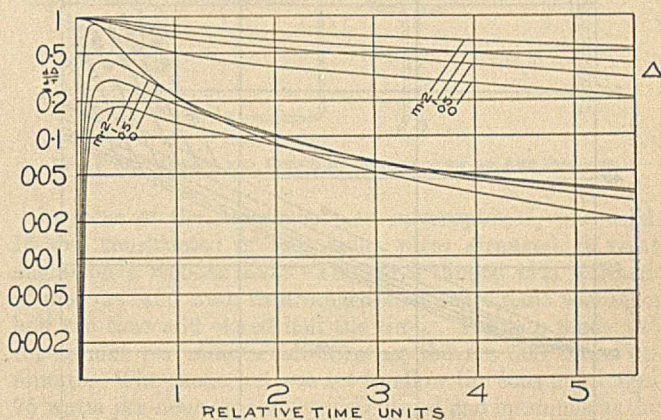


FIG. 5—UNACCOMPLISHED TEMPERATURE-CHANGE RATIOS (4 UPPER CURVES) WITH RATES OF (LOWER CURVES) VARIATION PER UNIT OF TIME FOR A POINT IN A SEMI-INFINITE SOLID INITIALLY AT UNIFORM TEMPERATURE.  $m$  DEFINES RELATIVE SURFACE RESISTIVITY

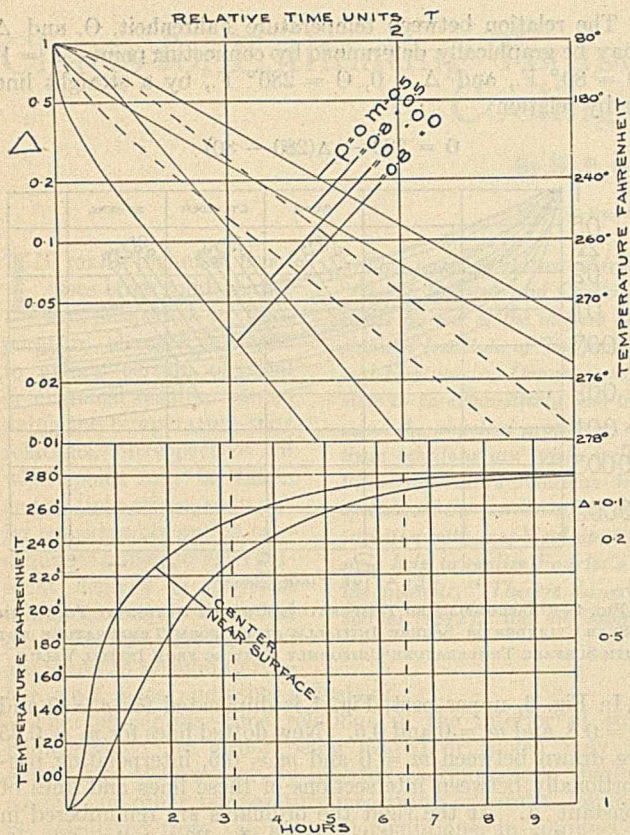


FIG. 6—ESTIMATED TEMPERATURE CURVES AT THE CENTER AND 1/4 INCH FROM SURFACE OF A SLAB OF RUBBER BEING HEATED FROM 80° TO 280° F.

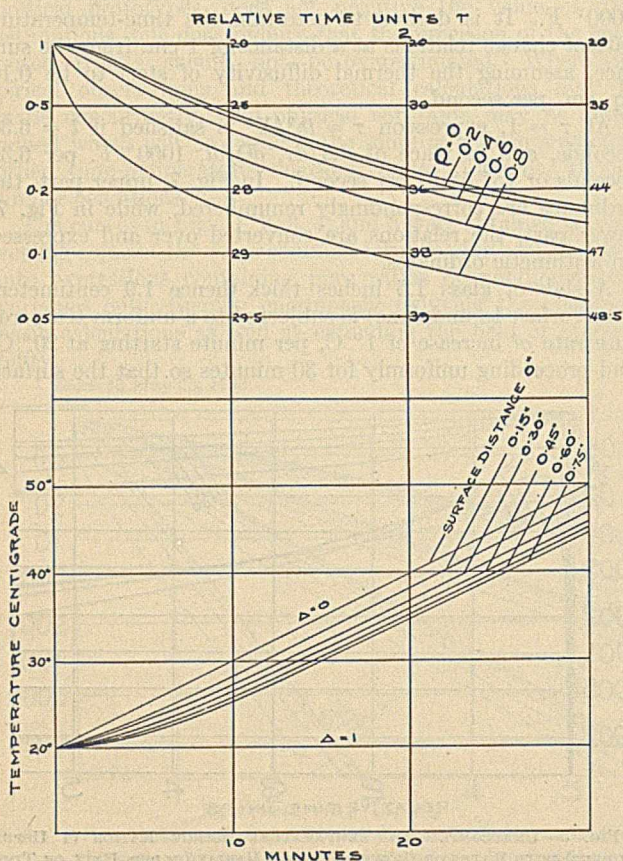


FIG. 8—TEMPERATURES IN A GLASS SLAB THE SURFACE TEMPERATURE BEING RAISED 1° C. PER MINUTE STARTING AT 20° C.

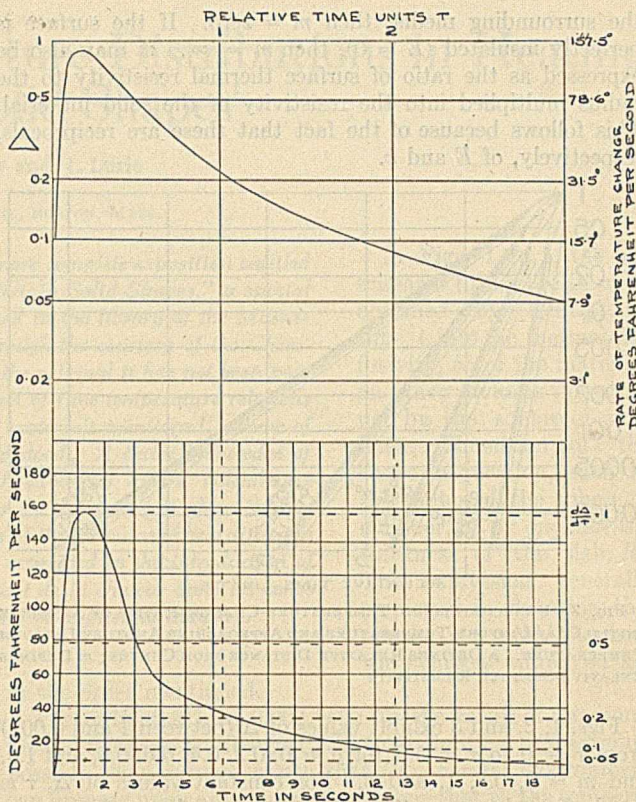


FIG. 7—RATE OF COOLING IN A STEEL INGOT 1 CM. FROM THE SURFACE—COOLING FROM 1100° TO 100° F.

then arrives at a temperature of 50° C. It is desired to ascertain the temperature-time relations at 0, 0.15, 0.30, 0.45, 0.60, and 0.75 inch from the surface—that is, at  $\rho = 1, 0.8, 0.6, 0.4, 0.2,$  and 0 from 0 to 30 minutes.

To satisfy equation  $\tau = th^2/R^2$  when  $\tau = 1, t$  must equal 600 seconds, or 10 minutes.

Fig. 8, upper part, presents Fig. 4 renumbered at  $\tau = 1, 2,$  and 3 to  $t = 10, 20,$  and 30, at which times the surface temperatures are by definition 30°, 40°, and 50° C., where  $\Delta = 1$  successively stands for 10°, 20°, and 30° C.

Fig. 8, lower part, presents the same relations on arithmetic ordinates. It will be noted here that after a short time the actual temperature differences between different layers equidistant from the midplane become uniform and the conditions approach a state of uniform flow.

It must be perfectly apparent from these examples that where temperature ratios are employed it is immaterial what temperature scale is used. In evaluation of  $\tau$  in the equation  $\tau = th^2/R^2,$  care must be taken that  $h^2$  is expressed in the same units as  $t$  and  $R^2.$  It should also be noted that Figs. 1 to 5, and upper parts of 6, 7, and 8 are expressed in arithlog ordinates—that is, the abscissas progress according to equal arithmetic increments, while the ordinates progress in a logarithmic order, equal increments represent equal ratio or percentage increases (or decreases). Because of the fact that many of the curves are nearly straight lines when plotted on arithlog paper, its use is particularly recommendable, especially if extrapolation is to be done. Figs. 6, 7, and 8, lower parts, are plotted on arithmetic ordinates. Both abscissas and ordinates progress by equal arithmetic increments.

On the occasion of the dedication of the Jesse Laboratory of Chemistry at Brown University on October 10, the degree of doctor of science was conferred on James W. McBain of the University of Bristol, who made the principal address. The degree of doctor of laws was conferred upon James R. Angell, president of Yale University.



# Experiments on the Arc Process for Nitrogen Fixation<sup>1</sup>

By Edgar D. McCollum and Farrington Daniels

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THE fixation of nitrogen by the arc process is a most alluring problem. It appeals to the research chemist because the present limits of efficiency (approximately 1 gram atom of fixed nitrogen per kilowatt-hour) are not established by theoretical deductions,<sup>2</sup> and because the electrochemistry of gases has received a new impetus in the recent development of the field of atomic structure. It appeals also to the industrial chemist because the raw materials—air, water, and gravity—are cheap and because the labor costs are remarkably low.

The problem can be solved and the limits of efficiency can be established only after years of fundamental research in the fields of electricity, photochemistry, and atomic structure. It seemed worth while, however, to perform a few experiments in which the variables were carefully limited in order to test out certain procedures which it was thought might increase the efficiency.

It is important to point out that in the case of stable, efficient arcs the practical problem lies in the quick removal of the nitric oxide before decomposition can set in, and it is immaterial whether the nitric oxide is formed in a purely thermal equilibrium, by electronic or ionic impact, or by photosynthesis. One of the simplest ways of quickly removing the products consists in blowing the air through the arc very rapidly. There are two limits to this procedure—first, the extinguishing of the arc, and, second, the difficulty of recovering the oxidized nitrogen when its concentration is low.

The second objection may be overcome by dispensing with the ordinary absorption towers filled with liquids and adsorbing the nitrogen peroxide with silica gel.<sup>3</sup> Since the cost of absorption in present practice constitutes about one-quarter of the total cost of fixing nitrogen by the arc process, the experiments seemed particularly worth while.

## APPARATUS AND PROCEDURE

The apparatus is shown in Fig. 1. The chamber, *A*, was made of Pyrex glass 5 cm. in diameter and 100 cm. long. The electrodes, *E*, were placed in side tubes, fused to the main tubes. The side tubes were long enough so that an airtight joint could be made with rubber tubing without danger of heating the rubber. The air was previously dried through two washing bottles of sulfuric acid and two towers of sodium hydroxide sticks. It was introduced into the arc from below by means of a 5-mm. glass tube at right angles to the electrodes. The end of the glass tube was placed 3 mm. from the electrodes and remained in the same position throughout all the experiments. The electrodes, of 3-mm. steel rods, were touched together to start the arc and then drawn apart to a distance of 5 mm. in all the experiments. The flowmeter, *F*, was calibrated in liters of air per minute, passing into the arc.

<sup>1</sup> Received April 16, 1923.

<sup>2</sup> Thermodynamical calculations such as given in Haber's "Thermodynamics of Technical Gas Reactions," p. 267, are open to considerable suspicion as regards the temperature. In fact, one cannot speak properly of the temperature of an arc in a quantitative sense.

<sup>3</sup> McGavack and Patrick, *J. Am. Chem. Soc.*, **42**, 946 (1920).

*Liquid nitrogen peroxide may be made on a laboratory scale from air in an electric arc with the help of silica gel. No improvement in the chemical efficiency of the arc was obtained by using rapid air currents, by interrupting the arc, or by changing the character of the arc with condensers. Better yields were obtained at high voltages.*

The nitrogen peroxide was collected in a weighed tube of silica gel, *S*, 2 cm. in diameter, a tube of glass wool, *G*, serving to trap particles coming from the disintegration of the electrodes. A second tube of silica gel and

a wash bottle were placed after tube *S*, but they showed at all times that the absorption in the first tube was complete. Most of the nitrogen peroxide was absorbed in the first 10 cm. of the tube, as shown by the brown color. Connections were made with overlapping glass joints and de Khotinsky cement. The increase in weight of the silica gel tube gave directly the number of grams of nitrogen peroxide. This weight was checked occasionally by heating the silica gel in a current of air. The loss in weight was always equal to the gain in weight previously observed.

The wattage throughout all the experiments was kept constant by adjusting the core of a choke coil, *C*, until the wheel of the watt-hour meter, *M*, made 6 revolutions per minute. This operation required close attention. Since each revolution of the wheel corresponded to 5/24 watt-hour, the energy input was 75 watts per hour. Most of the experiments were continued for an hour, giving usually about 1 gram of nitrogen peroxide, and the total energy consumed was read directly on the watt-hour meter. The current was measured with a hot wire ammeter in series with the arc.

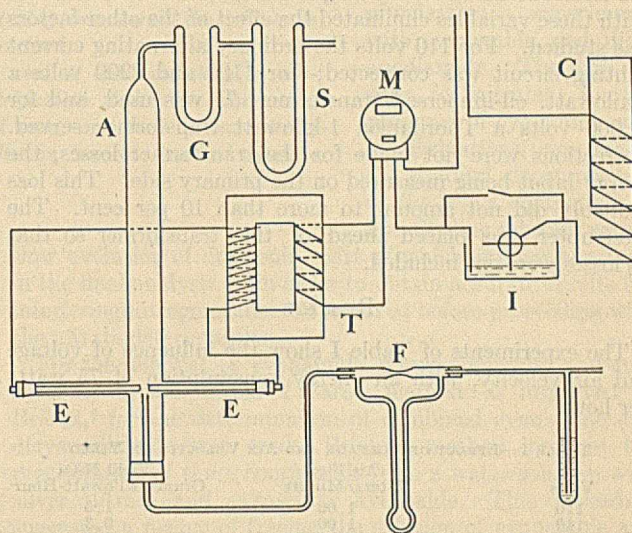


FIG. 1—APPARATUS FOR FIXATION OF NITROGEN BY ARC PROCESS

In some of the experiments an interrupter, *I*, was used. It was constructed of four stout wires arranged at right angles on a wooden hub. The wires dipped into a trough of mercury and were so arranged that the circuit was open half the time and closed half the time. The hub made 125 revolutions per minute, interrupting the arc 500 times per minute. The choke coil was set to allow the consumption of 75 watts per hour on continuous current and inasmuch as the current was flowing during only one-half of the time the experiment was allowed to run for a longer time. The actual energy consumption was read directly on the meter. In using

the interrupter the air flow was such as to sweep the products of the arc away from the electrodes while the arc was extinguished. One liter of air was passed through the 5-mm. tube in 1 minute. The cross section of the tube was 0.1963 sq. cm., giving a linear velocity to the gas of 1000/0.1963, or 5102 cm. per minute. The arc was out for 0.002 minute. The gas moved 10 cm. during this time. Since the height of the arc was between 2 and 3 cm. all the gas must have been removed from the region of the arc while the current was off, even allowing for spreading out of the air after leaving the nozzle.

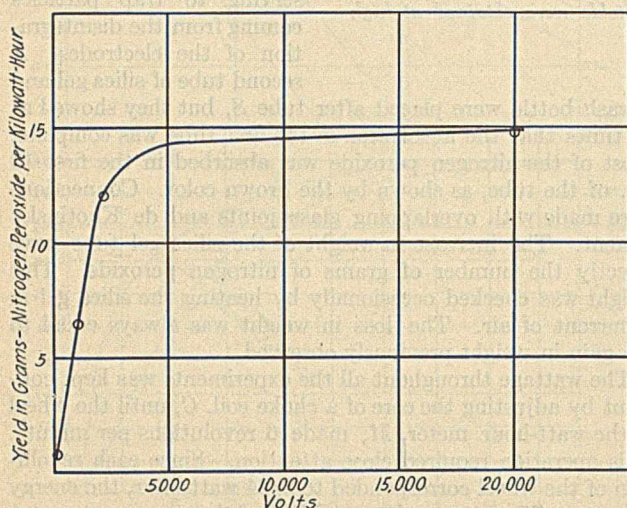


FIG. 2—RELATION BETWEEN VOLTAGE AND YIELD OF NITROGEN PEROXIDE

This apparatus made it possible to keep constant the energy input (75 watts per hour), the electrode material, the electrode distance, the air pressure, and the stream lines. With these variables eliminated the effect of the other factors was studied. For 110 volts the ordinary alternating current lighting circuit was connected; for 1100 and 2200 volts a 2-kilowatt, oil-immersed transformer, *T*, was used, and for 20,000 volts a Thordarson 1-kilowatt transformer served. Corrections were not made for the transformer losses, the energy input being measured on the primary side. This loss probably did not amount to more than 10 per cent. The interrupter was placed ahead of the transformer so that its losses were not included.

### RESULTS

The experiments of Table I show the influence of voltage and air velocity, with an energy consumption of 75 watts per hour.

TABLE I—EFFECT OF VOLTAGE AND AIR VELOCITY ON YIELD

Volts	Air Flow Liters/Minute	Yield $N_2O_4$ Grams/Kilowatt-Hour
110	1.00	1.5
110	1.00	0.3
1100	0.48	7.5
1100	0.90	7.9
1100	0.91	7.6
1100	0.94	4.9
1100	1.00	4.8
1100	1.00	7.5
1100	Fast	5.0
1100	Fast	8.2
1100	Fast	5.0
2200	1.00	12.3
2200	1.00	12.8
2200	1.00	10.2
2200	1.00	13.3
20,000	0.95	9.0
20,000	1.00	12.8
20,000	1.00	15.8
20,000	1.10	14.4
20,000	1.30	16.1

The agreement between experiments performed under supposedly constant conditions is not entirely satisfac-

tory, but these variations seem to be a failing common to all similar investigations, due possibly to slight fluctuations in the arc. Average values are, however, significant.

The 110-volt, 1100-volt, and 2200-volt arcs were yellow in color, but the 20,000 volt arc was whitish. The current with the 1100-volt arc was 0.7 ampere and with the 20,000 volt arc, 0.2 ampere. It is obvious that the power factor was low on account of the large amount of inductance in the circuit.

In Table II are shown the influence of various changes in the arc. In all these experiments the energy input was 75 watts per hour and the voltage 20,000.

TABLE II—EFFECT OF CHANGES IN ARC

DESCRIPTION OF ARC	Flow Liters/Minute	Yield $N_2O_4$ Grams/ Kilowatt-Hour
Spark discharge	0.95	2.0
	0.97	4.8
	1.00	4.9
Small condenser, blue spark	0.95	12.8
	1.00	8.9
	Fast	8.1
Large condenser, fat blue spark	Very slow	Low
	1.00	Low
Large condenser, 115 watts, yellow	1.00	4.2
Ozonized air used, white arc	1.00	11.4
	1.00	14.7
Interrupted arc, white	0.95	17.4
	1.00	15.9
	1.00	14.0
	1.00	13.5
	1.00	13.4

With large electrodes the yields decreased, and in fact with electrodes of too large cross section the thermal conduction was so great as completely to prevent the maintenance of an arc at the low wattages. If the electrodes were too small, on the other hand, they were melted by the arc. Terminals of stout platinum wire were fused at once.

Several experiments with direct current at 110 volts gave low yields which were about the same as those with the alternating current at 110 volts.

Since the second silica gel tube showed no increase in weight, it was assumed that the recovery of the fixed nitrogen was complete. The first silica gel tube returned to its original weight after heating to 350° C., in a slow stream of air (1 or 2 cc. per minute), and no nitric acid was observed either in the connecting tubes or in the tube surrounded by ice and salt in which the nitrogen peroxide was liquefied. These facts showed that all the fixed nitrogen was removed as nitrogen peroxide, even though some nitric acid may have been formed from the water on the silica gel.

The most important feature of the investigation consisted in keeping the energy input constant throughout the experiments. The maximum yield of 16 grams of nitrogen peroxide, or 22 grams of nitric acid per kilowatt-hour, is only about a third of the yield frequently obtained with large arcs in industrial practice.

### CONCLUSIONS

Adsorption with silica gel offers an excellent method for the recovery of oxides of nitrogen from the arc, since in this way nitrogen peroxide may be removed from rapid air currents at low concentrations. By heating the silica gel the concentrated nitrogen peroxide may be recovered ready for liquefaction, or for absorption in water to give concentrated nitric acid. The silica gel is then ready for further adsorption.

The yield of nitrogen peroxide per kilowatt-hour increases rapidly with the voltage up to a few thousand volts, after which further increase in voltage does not greatly affect it. The relation between voltage and yield per kilowatt-hour, for an energy input of 75 watts per hour in the apparatus described, is shown in Fig. 2. The curve is roughly of the exponential type and is similar to saturation curves obtained

in certain ionization experiments. It suggests that possibly an increase in voltage increases the fraction of energy which can be made to do chemical work, but that some other influence, such as concentration, or possibly an intermediate step of slow velocity, limits the production for the larger yields.

Small variations in the velocity of the air through the arc do not affect the yield within the experimental range studied. When the velocity is high enough to render the arc unstable the yield decreases appreciably. At very low velocities it is to be expected that the yield would decrease. Cramp and Hoyle<sup>4</sup> in an exhaustive study of the arc found that increasing the velocity of air through the arc increased the yield of nitrogen peroxide per ampere up to a maximum and then decreased it. It is important to point out, however, that their results were not on the basis of yield per given

energy input, but on the basis of yield for a given current.

Haber and Platou<sup>5</sup> found that increasing the velocity of air from approximately 0.5 liter per minute to 2 liters per minute increased the yield of nitric acid about one-third.

Interrupting the arc so as to sweep out the gases from an extinguished arc does not give increased yields. This fact shows that after the current is shut off the kinetic energy of the molecules is not decreased instantaneously to a condition (temperature) at which the nitric oxide is stable.

Spark discharges give less nitrogen peroxide per kilowatt-hour than arcs. The use of condensers is disadvantageous.

No increase in yield results from previously ozonizing the air.

Pure nitrogen peroxide may be readily obtained from air on a small scale with the use of silica gel in connection with an electric arc.

<sup>4</sup> *J. Inst. Elec. Eng.*, **43**, 319 (1909).

<sup>5</sup> *Z. Elektrochem.*, **16**, 802 (1910).

## Determination of Nitrate Nitrogen<sup>1</sup>

### In the Presence of Cyanamide and Some of Its Derivatives

By Kenneth D. Jacob

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**I**N CONNECTION with investigations on the rate of nitrification of commercial calcium cyanamide<sup>2</sup> and some of its derivatives in the soil an accurate method for the determination of nitrate nitrogen in the presence of these compounds is desired. Of the numerous methods proposed for the estimation of nitrate nitrogen, alone or in the presence of other forms of nitrogen, those based upon colorimetric or reduction procedures have as a rule proved the most satisfactory. Colorimetric methods give accurate results when the quantity of nitrate present is comparatively small, their relative accuracy decreasing as the amount of nitrate increases. It is also often difficult to obtain a colorless solution of the nitrate, especially with soils containing considerable organic matter and soluble salts. Of the reduction methods that using Devarda's alloy in dilute sodium hydroxide solution has under ordinary conditions given consistent and accurate results in the hands of different investigators, as shown by the excellent work of Allen<sup>3</sup> and of Davisson.<sup>4</sup> While the method gives satisfactory results in the presence of considerable soil organic matter, it is unreliable in the presence of cyanamide and many of its transformation products. Modifications of the Allen method which eliminate these interfering substances are here presented.

Preliminary experiments on the recovery of added nitrate nitrogen from mixtures containing cyanamide, urea, dicyanodiamide, or guanlylurea sulfate, by reduction with Devarda's

*Cyanamide and certain of its derivatives interfere in the determination of nitrates by reduction with Devarda's alloy.*

*Cyanamide, dicyanodiamide, and guanlylurea are quantitatively removed by precipitation with silver sulfate. Urea, if present, is converted into ammonia by the action of urease and the nitrogen contained in the urease extract removed with silver sulfate.*

*After elimination of the interfering compounds the nitrate is determined by the Devarda alloy method.*

*These analytical methods were used at this laboratory in connection with a series of soil nitrification studies on cyanamide, dicyanodiamide, guanlylurea, and urea, and have given entirely consistent and satisfactory results on several hundred separate analyses.*

alloy, gave in all cases results that were from 10 to 20 per cent above the theoretical. This fact had previously been observed by Cowie<sup>5</sup> in the course of nitrification experiments with cyanamide and dicyanodiamide. The high results for nitrates, in the presence of cyanamide and its derivatives, are due to the gradual decomposition of the latter compounds in hot alkaline solution with a

slow evolution of ammonia, part of which appears as nitrate in the final analysis. In order to obtain accurate results the interfering nitrogen must be removed before proceeding with the nitrate determination.

For the removal of cyanamide, dicyanodiamide, and guanlylurea, an adaptation of Caro's method, as improved by Brioux,<sup>6</sup> for the determination of combined cyanamide and dicyanodiamide was used. Brioux's method involves the precipitation of these compounds from a water solution with silver nitrate and potassium hydroxide. This procedure suggested a means of freeing the solution of cyanamide and dicyanodiamide, but silver nitrate could not be used as a precipitant because it introduced additional nitrate nitrogen. By using 100 cc. of a saturated solution of silver sulfate (containing about 0.75 gram Ag<sub>2</sub>SO<sub>4</sub>) the interfering nitrogen from a solution containing as much as 50 mg. of cyanamide, dicyanodiamide, or guanlylurea sulfate is satisfactorily removed. The interference due to the presence of urea is also reduced, but is not completely removed by this procedure.

Urea may be completely hydrolyzed<sup>7</sup> to ammonia and

<sup>1</sup> Received June 18, 1923.

<sup>2</sup> Hereafter referred to as cyanamide.

<sup>3</sup> *THIS JOURNAL*, **7**, 521 (1915).

<sup>4</sup> *Ibid.*, **10**, 600 (1918).

<sup>5</sup> *J. Agr. Sci.*, **9**, 113 (1919).

<sup>6</sup> *Ann. sci. agron.*, **27**, Pt. 1, 241 (1910).

<sup>7</sup> Fox and Geldard, *THIS JOURNAL*, **15**, 743 (1923).

carbon dioxide within a very short time by the action of the enzyme urease present in jack-bean flour. This procedure is effective in removing the interfering urea, since the ammonia formed can be easily removed by distillation before determining the nitrate. However, the extract of jack-bean flour itself contains nitrogen compounds which, on boiling with dilute sodium hydroxide, slowly evolve ammonia. The extract from 170 mg. of jack-bean flour, analyzed for nitrate nitrogen by Allen's<sup>2</sup> method, showed 0.39 mg. of nitrogen appearing as ammonia and 0.62 mg. as nitrate. The interfering nitrogen from the jack-bean flour extract is almost completely removed by precipitation with silver sulfate and potassium hydroxide, as shown later.

#### ANALYTICAL METHODS

1. **NITRATE NITROGEN IN ABSENCE OF INTERFERING COMPOUNDS**—This method is essentially that devised by Allen. A suitable aliquot of the solution containing the nitrate is measured into an 800-cc. Kjeldahl flask, 5 cc. of 20 per cent sodium hydroxide are added, and the total volume is made up to 350 cc. The flask is connected to a distilling apparatus, fitted with an efficient type of scrubber bulb, and boiled until 300 cc. of distillate collect in the receiver. This removes all ammonia, either free or combined. To the 50 cc. of solution remaining in the flask are added 200 cc. of water and 1.5 to 2 grams of nitrogen-free Devarda's alloy (about 60 mesh). The flask is immediately connected with the distilling apparatus, and 200 cc. are distilled into a known quantity of 0.1 or 0.05 *N* sulfuric acid, in the course of about 1 hour. The nitrogen, as ammonia, found by titrating the excess sulfuric acid with 0.05 *N* sodium hydroxide, using methyl red as an indicator, represents the nitrate present in the original aliquot.

The Kjeldahl flasks should be free from all traces of Devarda's alloy or zinc before distilling off the original ammonia; otherwise some of the nitrate may be reduced and thus fail to appear in the final nitrate determination.

2. **MODIFICATION FOR NITRATE NITROGEN IN PRESENCE OF CYANAMIDE, DICYANODIAMIDE, AND GUANYLUREA**—To a measured sample containing these forms of nitrogen are added 100 cc. of a saturated solution of silver sulfate and 10 cc. of a 15 per cent solution of potassium hydroxide. The precipitate is allowed to stand for about 1 hour, with frequent stirring, and is then filtered directly into an 800-cc. Kjeldahl flask. The precipitate is washed six times with 10-cc. portions of water, 5 cc. of 20 per cent sodium hydroxide are added to the flask, and the total volume is made up to about 350 cc. After distilling off the ammonia the nitrate nitrogen is determined as in the preceding method. Urea is only partly removed by this procedure.

Blank determinations should be run on all samples of silver sulfate, as this compound, unless especially purified, usually contains an appreciable quantity of nitrate.

3. **MODIFICATION FOR NITRATE NITROGEN IN PRESENCE OF UREA**—A neutral aliquot of the original solution containing urea, nitrate, and other forms of nitrogen is treated with 10 cc. of a neutral 2 per cent extract of jack-bean flour and allowed to stand for 1 hour. At the end of this time the enzyme urease will have converted the urea present into carbon dioxide and ammonia. In order to free the solution of the nitrogen added in the jack-bean extract, it is treated with silver sulfate and potassium hydroxide solutions as in the previous procedure, and the nitrate nitrogen is determined as usual, after first distilling off the ammonia. Cyanamide, dicyanodiamide, and guanylurea are also removed by this procedure.

#### EXPERIMENTAL RESULTS

In obtaining the data the distillations were carried out on an ordinary Kjeldahl rack, using the scrubber distilling bulb

described by Davison,<sup>3</sup> the bulb, condenser tube, and adapter being made of Pyrex glass and thus eliminating danger of alkali from the glass parts.

All the results have been corrected for the blank on reagents, and, in the case of soil extracts, the nitrate nitrogen present in the soil. The soil used was a Susquehanna loam that had been under cultivation as a garden for about 15 years, and contained a comparatively large quantity of organic nitrogen.

In order to determine to what extent cyanamide, dicyanodiamide, urea, and guanylurea interfere in the usual method for determining nitrates by reduction with Devarda's alloy, two sets of analyses were made, one using these compounds in water solution, and the other in the presence of soil extract. In the first case, quantities of the nitrogen compounds, each equivalent to 20.88 mg. of nitrogen, were weighed into separate Kjeldahl flasks, 350 cc. of distilled water added, and the usual nitrate determination was carried out. For the analyses in the presence of soil extract, quantities of the compounds, each equivalent to 20.88 mg. of nitrogen, were mixed with separate portions of 100 grams of air-dried soil and each sample was immediately extracted with 500 cc. of water. Aliquots equivalent to 8.35 mg. of added nitrogen were analyzed for nitrates by the procedure applicable in the absence of interfering compounds.

TABLE I—INTERFERENCE OF CYANAMIDE, DICYANODIAMIDE, UREA, AND GUANYLUREA IN DETERMINATION OF NITRATE NITROGEN BY REDUCTION WITH DEVARDA'S ALLOY

NITROGEN COMPOUND	Added Organic Nitrogen Appearing as Nitrate Nitrogen			
	A <sup>a</sup>		B <sup>b</sup>	
	Mg.	Per cent	Mg.	Per cent
Cyanamide	4.39	21.02	1.86	22.27
	4.23	20.26	1.51	18.08
Dicyanodiamide	3.76	18.01	1.42	17.00
	3.51	16.81	1.51	18.08
Urea	2.23	10.68	0.64	7.66
	2.15	10.29	0.65	7.78
Guanylurea sulfate	3.01	14.41	0.38	4.55
	2.90	13.88	0.38	4.55

<sup>a</sup> In pure solution. Added organic nitrogen = 20.88 mg.

<sup>b</sup> In the presence of soil extract. Added organic nitrogen = 8.35 mg.

Although the results given in Table I are not entirely comparable because of the varying quantities of organic compounds used in the two cases, they show that, even in the presence of comparatively small quantities of cyanamide and some of its derivatives, an appreciable portion of the organic nitrogen appears in the final analysis as nitrate.

In order to determine the efficiency of the method for the removal of interfering nitrogen due to the presence of cyanamide, dicyanodiamide, and guanylurea, quantities of these compounds, each equivalent to 20.88 mg. of nitrogen, were thoroughly mixed with 100-gram portions of air-dried soil, and the whole was immediately extracted with 500 cc. of water. Aliquots equivalent to 8.35 mg. of added nitrogen were treated as described under (2) of "Analytical Methods," with the following results:

The interfering cyanamide, dicyanodiamide, and guanylurea nitrogen can be removed practically to within the limits of experimental error by precipitation with silver sulfate and potassium hydroxide. The interference caused by the presence of urea is reduced by this procedure, but its removal is not complete.

In order to determine the efficiency of the method for the removal of interfering urea nitrogen, soil extracts containing urea were prepared in the same manner as those used in obtaining the results given in Table II. Aliquots equivalent to 8.35 mg. of urea nitrogen were analyzed by the method previously described for the removal of urea nitrogen.

The average results given in Tables II and III compare very favorably with respect to the removal of the added forms

TABLE II—EFFICIENCY OF METHOD FOR REMOVAL OF CYANAMIDE, DICYANODIAMIDE, AND GUANYLUREA

NITROGEN COMPOUND	(Added organic nitrogen = 8.35 Mg.)	
	Added Organic Nitrogen Appearing as Nitrate Nitrogen	Per cent
Cyanamide	Mg.	
	0.031	0.37
	0.023	0.27
	0.057	0.68
	0.031	0.37
Av.	0.035	0.42
Dicyanodiamide	0.023	0.27
	0.031	0.37
	0.031	0.37
	0.040	0.47
	Av.	0.031
Guanylurea sulfate	0.065	0.78
	0.098	1.17
	0.040	0.47
	0.048	0.57
	Av.	0.063
Urea	0.452	5.41
	0.528	6.32
	Av.	0.490

of organic nitrogen. In order to determine the efficiency of the procedures as regards the recovery of added nitrate nitrogen in the presence of the organic nitrogen compounds, soil extracts were prepared in the same manner as those previously used. Aliquots containing 3.89 mg. of added nitrate nitrogen in the form of potassium nitrate and 8.35 mg. of added organic nitrogen were analyzed by one of the procedures dependent upon the nature of the organic nitrogen present.

TABLE III—EFFICIENCY OF METHOD FOR REMOVAL OF INTERFERING UREA-NITROGEN

(Added urea nitrogen = 8.35 mg.)		
Added Urea Nitrogen Appearing as Nitrate Nitrogen	Per cent	
Mg.		
0.092	1.10	
0.045	0.53	
0.019	0.22	
0.019	0.22	
Av.	0.027	0.33
	0.040	0.48

TABLE IV—RECOVERY OF NITRATE NITROGEN IN PRESENCE OF CYANAMIDE AND SOME OF ITS DERIVATIVES

(Added nitrate nitrogen = 3.89 mg., added organic nitrogen = 8.35 mg.)			
ORGANIC NITROGEN COMPOUND	Added Nitrate Nitrogen Recovered	Per cent	
None	Mg.		
	3.930	101.03	
	3.920	100.77	
	Av.	3.925	100.90
Cyanamide	3.894	100.10	
	3.928	100.97	
	3.955	101.67	
	3.898	100.21	
	Av.	3.919	100.74
Dicyanodiamide	3.932	101.08	
	3.974	102.16	
	3.879	99.71	
	3.960	101.80	
	Av.	3.936	101.19
Guanylurea sulfate	3.896	100.16	
	3.852	99.02	
	Av.	3.874	99.59
Urea	3.886	99.89	
	3.877	99.66	
	3.919	100.74	
	Av.	3.894	100.10

## Colloidal Copper Hydroxide as a Fungicide<sup>1</sup>

By Henry D. Hooker, Jr.

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AT PRESENT there is no entirely satisfactory fungicide available. The two most important ones are Bordeaux and lime-sulfur, but both burn the foliage under certain climatic conditions, and neither is remarkable for its sticking or spreading properties. Bordeaux is difficult to prepare correctly and the ready-made mixtures on the market have not proved ideal. Lime-sulfur does not control some fungus diseases, such as apple blotch, and consequently fruit-growers must supplement lime-sulfur spraying by subsequent applications of Bordeaux where this disease is prevalent. Lime-sulfur is, moreover, a most disagreeable material to handle.

It was thought that a colloidal copper compound would prove an ideal fungicide. If a material having a positive electrical charge could be prepared, it should have in colloidal suspension the sticking and spreading qualities of lead arsenate. It was thought that the burning properties of Bordeaux might be eliminated by preparing an insoluble compound such as copper hydroxide in colloidal suspension because plant membranes are impermeable to colloids.

### PREPARATION OF COPPER HYDROXIDE

Colloidal copper hydroxide was prepared by using a modification of the method reported by Bradfield<sup>2</sup> for the preparation of colloidal iron hydroxide, aluminium hydroxide, and silicic acid. A 10 per cent solution of sodium hydroxide was added to a solution of copper sulfate with constant stirring until the supernatant liquid lost its color. Copper hydroxide was thrown down as a pale blue precipitate. An excess of alkali leads to the formation of a deep blue precipitate which changes on standing to black copper oxide.

This must be avoided and it is better to leave some copper sulfate in solution than to attempt to reach an end point. The mixture so prepared contains sodium sulfate, a small amount of copper sulfate in solution, and a precipitate of insoluble copper hydroxide which holds, probably by adsorption, a considerable amount of copper sulfate. The preparation of colloidal copper hydroxide depends on the removal of the electrolytes—namely, the copper sulfate and sodium sulfate in solution and likewise a large part of the adsorbed copper sulfate. This was accomplished by agitation and repeated washing by sedimentation. Distilled water was used.

When first thrown down by the addition of sodium hydroxide solution, a mixture was obtained that was far from homogeneous. This was pumped under pressure with a hand pump through a spray nozzle from one receptacle to another, to break up the precipitate and render the mixture as homogeneous as possible. This procedure was repeated after every few washings. The mixture was transferred to a tall glass vessel and allowed to settle for 24 hours. The supernatant liquid was siphoned off, distilled water was added, and the whole was mixed thoroughly by vigorous stirring. After a dozen such washings by sedimentation practically all the free salt was removed. As long as the copper hydroxide was washed in relatively small volumes of water—50 parts of water by weight to one of copper hydroxide—the supernatant liquid remained clear. After the free salt had been removed, the volume of wash water was increased to 200 parts of water by weight to 1 part of copper hydroxide, and the process of washing by sedimentation continued. After several washings the precipitate settled, leaving an opalescent, supernatant liquid. This contained a very small amount of copper hydroxide, which settled out after standing for

<sup>1</sup> Received July 23, 1923.

<sup>2</sup> *J. Am. Chem. Soc.*, **44**, 965 (1922).

several days. As the washing was continued the amount of copper hydroxide remaining in suspension after the settling of the larger particles increased until what might be termed an incipiently colloidal solution was obtained which contained 1 part by weight of copper hydroxide in 1000 of water. At this concentration and dispersion the solution foamed readily on shaking. This was the maximum concentration and dispersion obtained by the process described. The material so prepared is a delicate robin's-egg blue by reflected light and blue-green by transmitted light. The copper hydroxide remained in suspension for several weeks, but the solution became stratified.

By centrifuging in a supercentrifuge the copper hydroxide is thrown out. This may be ground up with small amounts of water, resuspended, and shaken according to the Bradford procedure. After centrifuging a few times a true colloidal solution can be prepared.

Various modifications of this method might be suggested. It would undoubtedly require fewer washings to prepare colloidal copper hydroxide from a monovalent salt such as copper chloride. Several devices might be used to remove larger percentages of water from the copper hydroxide than is possible by sedimentation, thus making each washing more thorough. The addition of small amounts of acetic acid will peptize the copper hydroxide. The object of this work, however, was to prepare colloidal copper hydroxide from the cheapest materials by the simplest procedure. If a supply of soft water had been available, this would have been used instead of distilled water, thus reducing still further the cost of manufacture.

#### SPRAYING EXPERIMENTS

Two distinct types of copper hydroxide were used in the spraying experiments. One was a sediment from which all free soluble salts had been washed, but which showed no tendency to go into colloidal suspension. When washed in a large volume of water it settled out quickly, leaving a clear supernatant liquid. The other was an incipiently colloidal preparation purified as far as possible by the sedimentation method. This material remained in suspension for a long period and foamed when shaken.

Experiments were carried out in a neglected apple orchard that had not been sprayed for several years. The materials were used in the following concentrations:

COPPER HYDROXIDE	Trees Sprayed	Concentration %	Parts by Weight of Water to 1 Part Cu(OH) <sub>2</sub>	Copper Used Compared with 3:4:50 Bordeaux %
<b>Sediment:</b>				
1st dilution.....	2	0.4	250	143.0
2nd dilution.....	1	0.2	500	71.5
3rd dilution.....	2	0.1	1000	35.8
4th dilution.....	4	0.05	2000	17.9
<b>Colloid:</b>				
1st dilution.....	1	0.076	1315	27.0
2nd dilution.....	2	0.038	2630	13.5
3rd dilution.....	3	0.019	5260	6.8

The trees sprayed were Ben Davis. A power spray was used and the material was applied with a spray gun. The first application was a calyx spray on May 11. This was followed by sprays on May 21 and June 4. On the two latter occasions lead arsenate was added at the rate of 3 pounds of powder to 100 gallons of spray. Fifteen trees in the same orchard were sprayed at the same time with 3:4:50 Bordeaux and fifteen others with 3:100 lime-sulfur. A large number of trees were left unsprayed as checks. The only water supply available for diluting the spray material was a muddy stock pond. This water was used, though clear water would have been preferable, as mud is a negative colloid and throws copper hydroxide out of suspension.

The early part of the season was characterized by cool, wet weather, particularly favorable to Bordeaux burning.

When the last spray was applied it was observed that all the apples in the trees sprayed with the copper hydroxide sediment had been burned, presumably by the first application. Contrary to expectations the first dilution of the colloidal preparation produced exceptionally severe burning; the second dilution gave burning approximately equivalent to the 3:4:50 Bordeaux; the lowest dilution produced very little burning, not much more than lime-sulfur. The first dilution of the sediment gave severe burning, though not so severe as the strongest concentration of the colloid; the second burned about equal to 3:4:50 Bordeaux; the third and fourth, slightly less. It was distinctly noteworthy that dilution of the colloidal preparation reduced burning to a greater extent than did similar dilution of the sediment.

On July 12 the fruit was removed from each of the sprayed plots and from check trees to determine the fungicidal value of the sprays. The unsprayed fruit showed both apple scab and apple blotch. Approximately 20 per cent of the fruit was diseased, 13 per cent by scab and 7 per cent by blotch. The fruit on all sprayed trees was clean, not a single sign of scab or blotch being found on any of the apples from trees sprayed with copper hydroxide. The trees treated with the first dilution of the sediment and of the colloid had lost all their apples, apparently as a result of the severe burning.

The fact which merits emphasis is that under the conditions of the experiment complete protection from both scab and blotch was afforded by the weakest concentration of the colloidal copper hydroxide used and that this spray produced very little burning, much less than 3:4:50 Bordeaux and very little more than lime-sulfur. The amount of copper used was one-fifteenth that used in 3:4:50 Bordeaux. These preliminary tests would indicate, therefore, that a great saving in the cost of fungicidal spray materials could be made by using prepared colloidal copper hydroxide. Should the results be confirmed by subsequent tests under a wide variety of climatic conditions, 1 pound of copper as colloidal copper hydroxide would suffice to spray 2 to 3 acres of apple orchard once. It is, of course, possible that an even more dilute concentration may give adequate protection and no burning.

Additional experiments on a small scale have shown that colloidal copper hydroxide can be mixed with nicotine sulfate. A colloidal solution containing 1 part of the hydroxide in 5000 parts of water was sprayed on one peach tree and on one cherry tree. This work was done with a hand pump and a rod with a disk nozzle. No evidence of burning on either kind of fruit could be found. However, no additional information concerning the fungicidal properties of copper hydroxide was obtained.

#### CONCLUSION

Preliminary experiments indicate that copper hydroxide prepared as a colloid is fungicidal to apple scab and apple blotch in concentrations of 1 part of hydroxide to 5000 of water. At this concentration it produced very slight burning. It has excellent sticking properties due to its positive charge and spreads well in dilute solution. It can be used in conjunction with lead arsenate and nicotine sulfate. Although it would be hazardous to estimate the cost of manufacture, it is clear that colloidal copper hydroxide would be much less expensive than either Bordeaux or lime-sulfur.

From Germany comes announcement of the death of P. Friedländer, privat-dozent for organic chemistry and technical organic technology in the Technical Hochschule at Darmstadt. Professor Friedländer is well known for his investigations on the chemistry of dyestuffs and for his work "Fortschritte der Teerfarbenfabrikation," which appeared in twelve volumes.

# Studies of the Activity of Organic Nitrogenous Compounds—II<sup>1,2</sup>

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THIS work may perhaps be characterized as an analysis of the alkaline permanganate method. In it an attempt has been made to follow the progress of the digestion and distillation by analyzing the digestion mixture at regular intervals and by collecting the distillate in fractions in each of which the ammonia was determined.

The procedure finally followed was the outgrowth of a lengthy study of the problem and of many attempts to develop a method as closely analogous as possible to the official technic. One plan tried out involved running the experiments in regular Kjeldahl flasks and sampling the contents at intervals. It was thought that satisfactory results could be obtained by assuming that the total nitrogen present in the system at any time equaled the amount originally present less the ammonia removed. Only after considerable work had been done and a number of other possibilities eliminated was it discovered that nitrogen escaped in some form other than ammonia (apparently as free nitrogen), which fact introduced appreciable errors into the results. It was found necessary actually to determine in each fraction both the ammonia in the distillate and the total nitrogen in the residue.

## APPARATUS

The apparatus consisted of twelve pairs of test tubes, 2.5 cm. in diameter and 25 cm. long, each tube being fitted with a perforated rubber stopper through which passed two pieces of glass tubing about 6 mm. in diameter. One of these reached almost to the bottom of the test tube and terminated in a bulb perforated with a number of holes which served to break up into small bubbles the air stream drawn through it, while the other was flush with the bottom of the stopper. One test tube in each pair served as a reaction vessel and the other as a receptacle for standard acid to catch the ammonia evolved, the outlet tube of the former connecting with the inlet tube of the latter.

## PROCEDURE

In making the determinations one-third of the amount of sample necessary to furnish 50 mg. of water-insoluble nitrogen—i. e., one-third of an official sample—was weighed into each reaction tube. The connection with the companion

*In a previous publication<sup>3</sup> it was shown that a more or less intimate relationship existed between the nitrogen present in an acid hydrolysate as amino acids and acid amides and that evolved as ammonia upon oxidation with alkaline permanganate solution as prescribed by the official methods of the A. O. A. C.<sup>4</sup>*

*In the present article the action of permanganate is further studied using two samples of protein and several of common base goods of the fertilizer trade. Previous work dealt only with the ultimate quantities of ammonia, acid amide, and amino nitrogen obtained upon decomposition. In the work herein reported an effort was made to ascertain whether or not any connection exists between the rates of decomposition of various materials and their fertilizer values. The study of the several factors influencing the results with the permanganate digestion was also undertaken.*

tube containing acid was then made and 40 cc. of an alkaline permanganate solution (one-third the official quantity) were introduced through the inlet tube, slight suction being applied to the outlet of the acid tube for the purpose. The reaction tubes were then thoroughly shaken and set in a water bath (95° C.) while the attached tubes were held outside of the bath by means of clamps.

In working with proteins it was found that complete solution was effected during the 15 minutes allowed for the temperature of the contents of the tubes to rise from that of the room to that of the bath. This procedure was arbitrarily followed with all the other materials, assuming that the alkali-soluble matter would be dissolved during this preliminary stage. Time was counted from this point and one tube removed every 5 minutes for 30 minutes, an interval corresponding to that specified for the digestion of the sample in the official A. O. A. C. methods. Each tube was removed with the acid-containing one attached and immediately cooled to room temperature to stop the reaction. The outlet of the acid-containing test tube was then attached to a suction pump to remove any ammonia remaining in the digestion mixture and the excess acid titrated as usual. The digestion residue was transferred to a volumetric flask, acidified with sulfuric acid, diluted to the mark, and used for the determination of total and amino nitrogen.

At the end of the 30 minutes, when the sixth pair of tubes had been removed, the remaining six were transferred to an oil bath. After 10 minutes one tube was taken out and another at the end of each subsequent 10-minute interval, so that the total time consumed in the experiment, exclusive of the preliminary "solution" period, was 90 minutes. The oil bath used during the last 60-minute stage was held at such a temperature (140° C.) that only a small amount of liquid remained in the last tube when it was removed. By this procedure its contents were subjected to the conditions prescribed by the official methods.

It must, of course, be admitted that this procedure, which differs markedly from that specifically fixed in the official method, may in some cases lead to very different results. The rather good agreement between the final values for the active insoluble nitrogen as determined by the two procedures indicates that such differences are but little in excess of those normally to be expected with the official method. The writers, therefore, feel confident that, in spite of the radical differences in technic, the conclusions drawn from the present work are applicable to the official procedure.

All determinations were made in duplicate and the duplicates agreed as well as could be expected.

For purposes of comparison, determinations using the same strength of alkali but omitting the permanganate were also

<sup>1</sup> Received July 27, 1923.

<sup>2</sup> Journal Article No. 25 from the Chemical Laboratory of the Michigan Agricultural Experiment Station. Published by permission of the Director of the Experiment Station. The material contained in this article was originally to be published in two papers, the second and third in the series. As such they were read by title at the Birmingham and Pittsburgh meetings, respectively, of the American Chemical Society.

<sup>3</sup> THIS JOURNAL, 13, 933 (1921).

<sup>4</sup> Assoc. Official Agr. Chem., Methods, 1920, p. 11.

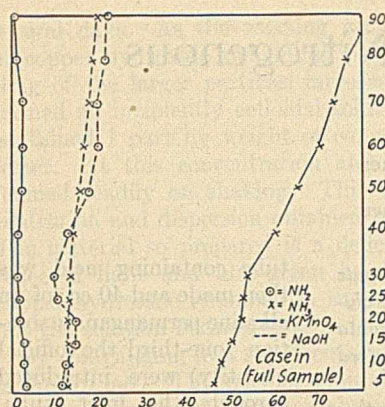


FIG. 1

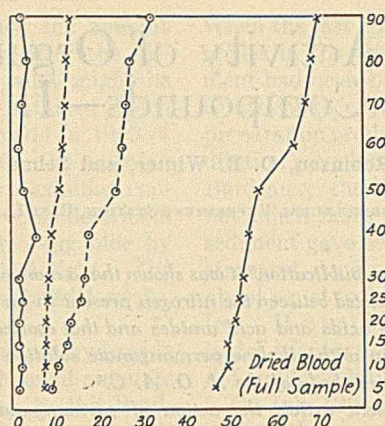


FIG. 2

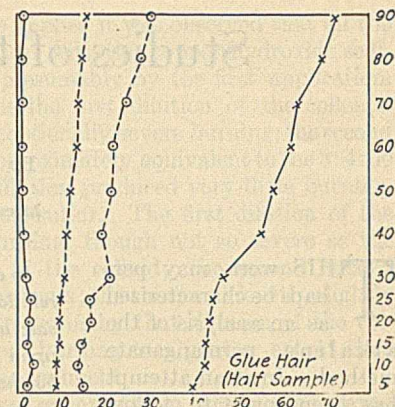


FIG. 3

made, thus making it possible to calculate the actual results due to the permanganate.

The results are shown in the accompanying figures.

#### EFFECT OF ALKALI ALONE AND OF ALKALINE PERMANGANATE

The chief result of the action of alkali on protein compounds is one of hydrolysis with the formation of ammonia and amino acids, the former being produced chiefly from acid amides, although there are some secondary reactions whereby some compounds other than acid amides are made to yield ammonia. While the relative amounts of ammonia and amino nitrogen produced by protein hydrolysis vary with different substances, the quantity of amino nitrogen is always much greater than the ammonia. In the most common animal proteins the ammonia formed during acid digestion amounts to about 5 to 10 per cent of the total nitrogen, while the amino fraction approximates 60 to 70 per cent. Data are not available on the alkaline hydrolysis of many materials, but these figures would be somewhat changed, the ammonia tending to increase at the expense of the amino nitrogen.

Inspection of the graphs illustrating the results of the action of alkali alone upon the materials used in the present work shows that the quantities of ammonia are unusually high, that the amino nitrogen values are low, and that their sum is usually not equal to the ammonia and amino nitrogen ordinarily found in protein. Hence it may be concluded that hydrolysis is incomplete under the conditions of these experiments. In general, both forms of nitrogen increase during the progress of the digestion and the maximum is not reached.

The permanganate graphs show an entirely different picture. Here the amino nitrogen is almost negligible in quantity and tends to decrease in amount as the digestion

progresses. In the case of the full sample of glue hair where the permanganate color was discharged at the end of 20 minutes, the amino nitrogen tends to increase, the curve assuming more closely the form of that for the alkaline digestion. With the full sample of cottonseed meal the same condition exists during the middle part of the experiment, but during the last 20 minutes an increased formation of ammonia is accompanied by a decrease in the amino nitrogen. While it is apparent that some of the ammonia in all cases is produced at the expense of the amino nitrogen, the lack of agreement between the total amounts produced indicates that this is not the whole story, but that the action of the permanganate is more deep-seated, producing ammonia from linkings not ammonified by alkali alone.

#### ACTION OF PERMANGANATE IN RELATION TO MEASUREMENT OF NITROGEN ACTIVITY

Two fundamental criticisms of the alkaline permanganate method have been made. It has been stated that results cannot be accurately duplicated because of the terminal conditions which deal with an incomplete reaction progressing with considerable rapidity and necessitating a control of conditions not ordinarily possible. It has also been shown that with substances which decolorize the reagent the results obtained are due to quite different causes than those secured with materials which do not decolorize the permanganate solution. The writers have stated in a previous paper<sup>3</sup> that the former criticism was of greater theoretical than practical importance. It does, however, become significant, as was stated in a later paper,<sup>5</sup> in cases where, because of foaming, the duration of the digestion and distillation is protracted beyond the specified 90 minutes. The curves herewith presented substantiate these statements.

<sup>5</sup> *J. Assoc. Official Agr. Chem.*, 5, 448 (1922).

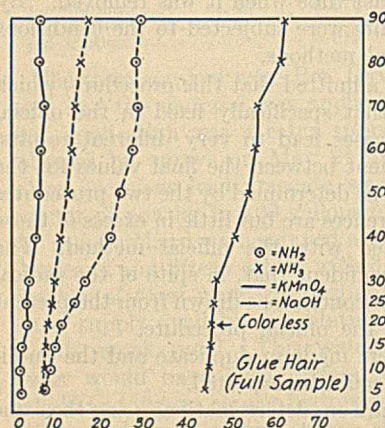


FIG. 4

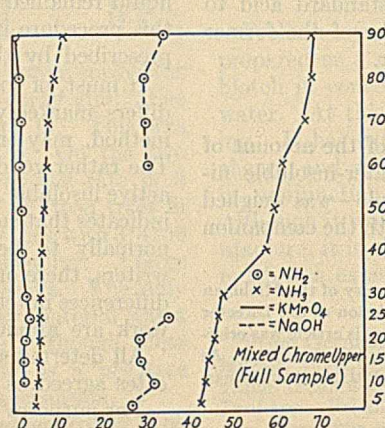


FIG. 5

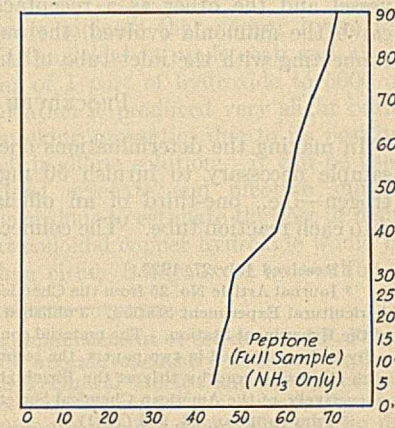


FIG. 6



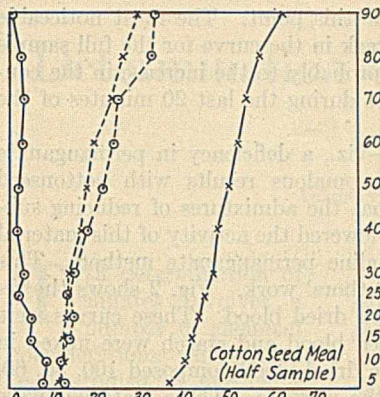


FIG. 7

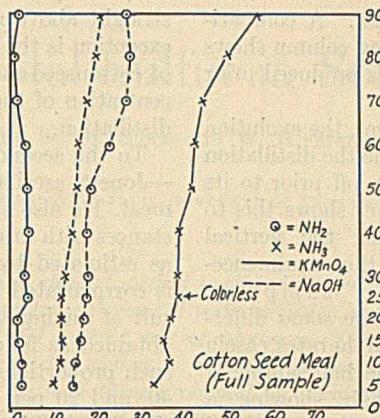


FIG. 8

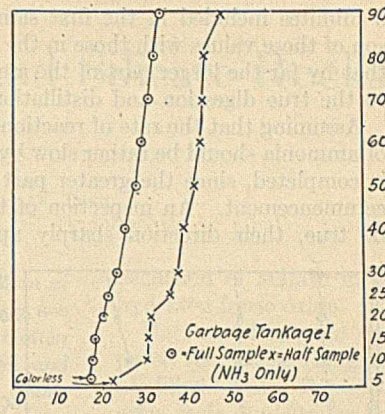


FIG. 9

The total quantity of ammonia produced, which is a measure of the activity of the materials under consideration, is the sum of two factors: (1) that formed during the preliminary digestion or "solution" period, and (2) that formed during the measured digestion and distillation periods. The former constitutes most of the ammonia in the first tube removed, while the latter is, of course, the rest of the ammonia collected in the other eleven tubes. The ammonia fraction may be further subdivided into that which is liberated by the alkali alone and that set free by the permanganate. With the exception of the "base goods" the values for the first portion vary between 5 and 12 per cent of the total nitrogen. The "base goods" showed 25 per cent ammonia in the first sample taken in the alkali digestion. This material was composed of garbage, beet slop, and leather, and had been mixed in the usual way with rock phosphate and sulfuric acid and allowed to stand in a den. The nature of the resulting product is problematical. Had the organic nitrogen been ammonified, it would, of course, have been washed out, as only the water-insoluble portion was used for this work. It is hard to conceive of a degradation product which would be so readily ammonified as this. With this exception the initial ammonia contents show nothing of interest or importance.

The quantities of ammonia produced up to the taking of the first sample are given in Column 4 of Table I. Column 5 shows the ammonia produced during the remainder of the digestion and distillation. It is a rather interesting fact that, by bringing the temperature up to the digestion point during 15 minutes and holding it there for 5 minutes, results are obtained which, with few exceptions, have the same relative magnitudes as those obtained by the official method, which requires 90 minutes to carry out. Many analysts assume that materials having 50 per cent or more of this

insoluble nitrogen in the active form are made from base goods of satisfactory quality. If a passing value of 30 per cent, instead of 50 per cent, were used, all the materials would pass by about the same margins that they do in the present official method.

TABLE I—ACTION OF PERMANGANATE ON ORGANIC NITROGENOUS COMPOUNDS

MATERIAL	(1) <sup>a</sup>	(2)	(3)	(4)	(5)
Casein	74.35	82.35	70.59	46.58	35.77
Dried blood	68.70	70.00	64.70	46.84	23.16
Glue hair	{ Full 67.45	62.25	55.78	43.93	18.32
	{ Half 66.66	72.00	62.35	39.94	32.06
Chrome uppers	{ Full 64.35	68.47	61.10	42.18	25.29
	{ Half 52.60	56.95	42.30	32.27	24.68
Cottonseed meal	{ Full 66.08	62.10	52.18	36.50	25.60
	{ I, full 28.38	33.47	29.19	17.28	...
	{ I, half 45.60	47.15	42.58	22.08	...
	{ II, full ...	25.10	23.31	16.40	...
	{ II, half ...	42.86	38.80	24.91	...
Tartar pomace	{ Full 33.79	34.24	29.76	14.43	...
	{ Half 42.06	46.69	38.48	26.40	...
Tobacco stem	{ Full 22.68	25.09	20.08	16.35	...
	{ Half 34.36	31.41	27.70	19.75	...
Base goods, I	{ Full 32.28	...	...	...	...
	{ Half 52.64	...	...	41.38	...

<sup>a</sup> (1) Active insoluble nitrogen, official method.  
 (2) Active insoluble nitrogen, step method.  
 (3) Active insoluble nitrogen, at 60 minutes.  
 (4) Ammonia formed during preliminary digestion plus ammonia present.  
 (5) Ammonia formed after preliminary digestion.

The influence of the initial ammonification is especially noticeable in the cases of the distinctly low-grade materials, garbage tankage, tartar pomace, and tobacco stems. Although both the slopes of the curves and the amounts of ammonia produced during the solution period are less than those in the high or medium grade, it is the initial ammonification factor that determines the final value. The importance of this will be taken up later.

The last column shows the ammonia liberated during the regular digestion and distillation periods less the first

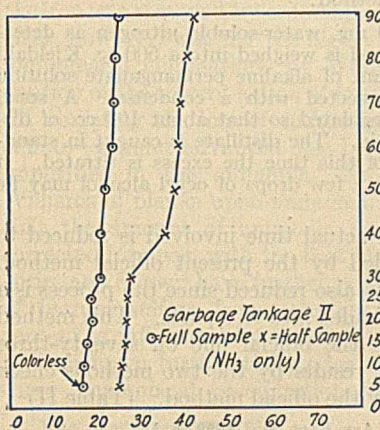


FIG. 10

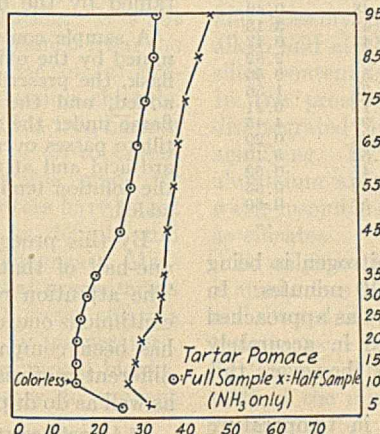


FIG. 11

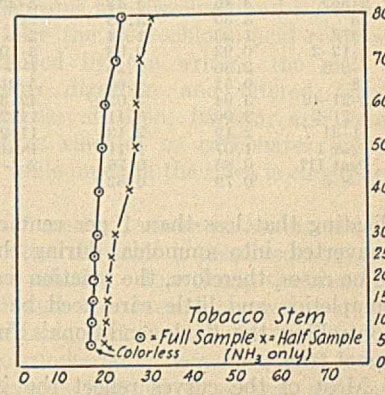


FIG. 12

5 minutes included in the first sample taken. A comparison of these values with those in the preceding column shows that by far the larger part of the ammonia is produced prior to the true digestion and distillation.

Assuming that the rate of reaction decreases, the evolution of ammonia should be rather slow by the time the distillation is completed, since the greater part is given off prior to its commencement. An inspection of the curves shows this to be true, their direction sharply approaching the vertical

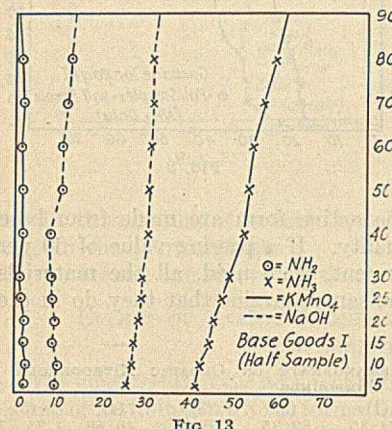


FIG. 13

—i. e., that at the end of the process the reaction is still progressing so rapidly that accurate results are not obtainable. In the cases of casein, both samples of cottonseed meal, and to a lesser extent the half sample of glue hair, the curves still deviate from the vertical axis, indicating that ammonia is still being given off rather rapidly (from 3 to 7 per cent during the last 10 minutes); while in the other cases the curves practically coincide with the vertical axis, in-

TABLE II—PER CENT OF ACTIVE INSOLUBLE NITROGEN AS DETERMINED BY THE OFFICIAL AND MODIFIED METHODS

Sample	Official Method	Modified Method	Sample	Official Method	Modified Method
1	1.08	1.05	144	1.26	1.31
146	0.42	0.47	148	0.46	0.46
150	0.20	0.21	153	0.54	0.61
162	0.51	0.53	169	0.42	0.39
172	0.30	0.33	182	0.22	0.23
208	0.93	1.02	388	0.11	0.12
389	0.18	0.19	396	0.42	0.44
404	0.30	0.32	412	0.38	0.40
415	0.13	0.14	417	0.81	0.77
419	0.22	0.23	420	0.19	0.19
425	0.20	0.20	455	0.62	0.64
465	0.48	0.55	476	0.61	0.64
478	0.23	0.24	480	0.35	0.37
481	0.36	0.37	483	0.27	0.29
487	0.14	0.16	495	0.40	0.42
500	0.43	0.45	501	0.67	0.69
502	0.28	0.29	505	0.18	0.20
508	0.17	0.17	512	0.40	0.43
515	0.52	0.45	523	0.39	0.42
712	0.17	0.18	716	0.57	0.58
717	0.19	0.20	721A	0.24	0.22
721B	0.41	0.42	723	0.19	0.19
725	0.28	0.29	726	0.13	0.14
728	0.49	0.48	730	0.48	0.49
731	0.31	0.30	24860	3.42	3.18
24862	3.46	3.42	5-22-1	0.47	0.47
15	3.30	3.38	11	2.93	2.82
3577	1.23	1.24	2-1-2	0.52	0.56
2-12-2	0.93	0.93	3-10-4	1.38	1.36
4-8-8	2.36	2.25	1-5-10	0.18	0.21
18	0.51	0.60	5-21-15	3.90	4.45
2-21-46	3.94	4.02	4213	0.28	0.29
6-21-2	3.06	3.41	11-21-1	4.52	5.10
11-21-7	2.19	2.13	11-21-8	0.47	0.52
Peat I	1.07	1.11	Peat II	0.62	0.65
Peat III	0.85	0.76	2-1-2	0.57	0.60
1-8-5	0.79	0.82	....	..	..

dicating that less than 1 per cent of the nitrogen is being converted into ammonia during the last 10 minutes. In some cases, therefore, the reaction evidently has approached completion and little care need be exercised in accurately controlling the final conditions. In others, however, this is not true.

Most of the curves reflect the increase in temperature with the commencement of the distillation, but are fairly

straight above and below this point. The most noticeable exception is the sharp break in the curve for the full sample of cottonseed meal, due probably to the increase in the concentration of the reagents during the last 20 minutes of the distillation.

To the second factor—viz., a deficiency in permanganate—Jones<sup>6</sup> ascribed the anomalous results with cottonseed meal. He also showed that the admixtures of reducing substances with dried blood lowered the activity of this material as estimated by the alkaline permanganate method. This is corroborated by the authors' work. Fig. 2 shows the result of mixing starch with dried blood. These curves were obtained as follows: Dried blood and starch were mixed in such proportions that the dried blood composed 100, 80, 60, 40, and 20 per cent of the mixture. These materials were then handled in the usual manner, the samples being weighed out on the basis of the insoluble nitrogen content. Increasing proportions of starch cause corresponding decreases in the activity of the dried blood until the amount of nitrogen ammonified is reduced from 60 to 20 per cent.<sup>7</sup>

Attention has been called to the fact that most of the ammonia is produced during the early stage of the digestion, and it has been pointed out that the sequence of materials when arranged in order of the percentages of nitrogen ammonified is the same whether based on the ammonia formed during the first 20 minutes or on the whole period of reaction. This suggested the possibility of modifying the present alkaline method so as to reduce the time and attention required. In previous attempts to accomplish this, stress was laid on the relative amounts of sample and reagent in trying to remedy the above-mentioned defects in the method.

The following suggested modification does not do this. The results by it are no more reliable than those obtained by the official procedure and whatever can be said in this respect for or against the one can be likewise said of the other. However, the results by the modified method appear to be just as valuable as those with the present official method, and they are obtained with considerable economy of time

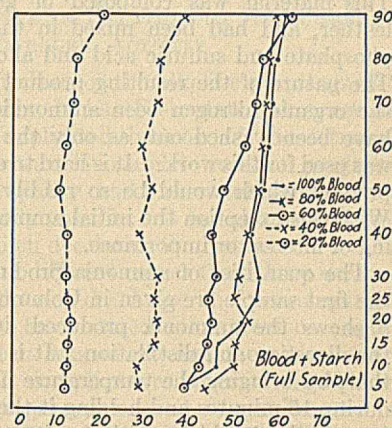


FIG. 14

and trouble. After several trials the following procedure has been selected as giving results comparable to those obtained by the official method:

A sample containing 50 mg. water-soluble nitrogen as determined by the official method is weighed into a 500-cc. Kjeldahl flask, the prescribed amount of alkaline permanganate solution added, and the flask connected with a condenser. A small flame under the flask is regulated so that about 100 cc. of distillate passes over in 45 min. The distillate is caught in standard acid and at the end of this time the excess is titrated. If the solution tends to foam a few drops of octyl alcohol may be added.

By this procedure the actual time involved is reduced to one-half of that demanded by the present official method. The attention required is also reduced since the process is a continuous one and not divided into two parts. This method has been compared with the official one on seventy-three different materials. The results by the two methods check as well as do duplicates by the official method. (Table II)

<sup>6</sup> Annual Report, Vermont Agr. Expt. Sta., 1899, p. 139.

<sup>7</sup> Work done by A. W. Lowell.

# Determination of Total Sulfur in Soils and Silicate Rocks<sup>1</sup>

By W. M. Shaw and W. H. MacIntire

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THE determination of sulfates involves a number of chemical considerations which have been studied in particular by Allen and Johnston,<sup>1,\*</sup> Blumenthal and Guernsey,<sup>3</sup> and Hirst and Greaves.<sup>8</sup>

Much difficulty has been encountered in making speedy and accurate determinations of total sulfur in soils. At its 1919 meeting the Association of Official Agricultural Chemists directed the junior author, as Referee for Soils, to study the problem. In connection with that study,<sup>10,11,12</sup> the present mode of procedure was developed.

Most soils are of low sulfur content and large charges are necessary to insure sufficient analytical quantities of barium sulfate. Assurance of complete combustion and absolute disintegration of the mass must be had. When these two requirements are met there is the further difficulty of insuring complete removal of the oxidized sulfur from the insoluble residue. In studying methods the authors endeavored to secure complete oxidation and removal of sulfates from the insoluble siliceous residue by boiling with concentrated nitric acid and filtering through a 10-cm. Büchner, the use of which facilitated washing of a thin layer of soil. No assurance was obtained that complete oxidation of native sulfur materials was effected. It was also found by the authors and their collaborators<sup>12</sup> that with longer periods of boiling of soil with nitric acid and subsequent replacement of nitric acid by hydrochloric acid, lower sulfate recoveries were obtained. It appeared that this inverse relationship of time to recovery was due, in part at least, to the interference of *barium*. The common occurrence of barium in soils was shown by Failyer.<sup>4</sup> It is obvious that this element will be dissolved by hydrochloric acid extractions of the melts secured by the several fusion methods.

The presence of iron and aluminium in hydrochloric acid solution has been considered detrimental to the accuracy of barium sulfate determinations. Williams<sup>19</sup> showed that sulfate determinations in soils were consistently higher if the iron was removed by ammoniacal precipitation. It is not clear, however, whether the higher results obtained from the ammoniacal eliminations by Williams are due to (a) prevention of the solvent action of ferric and aluminium chloride, (b) obviating the loss of sulfate from a double iron barium sulfate—a point advanced also by Talbot,<sup>17</sup> or (c) to sulfate impurities in the ammonia. No mention was made by Williams of blanks upon ammonia. The writers have found that the amount of ammonia used must be definite and corrected for, even with the best high-grade chemical. MacIntire and Shaw<sup>12</sup> have further pointed out that precipitation of barium sulfate from solutions of equal ferric chloride content is influenced by concentration and by temperature. It was shown further that, after applying empirical blanks, three ammoniacal precipitations are necessary to prevent

*A rapid and efficient method is offered for the determination of total sulfur in large charges of soils by fusion at a relatively low temperature and without use of platinum. Complete oxidation and absolute disintegration is assured. Aqueous extraction and filtration of the melt insures removal of aluminium, iron, manganese, and alkali earths, and eliminates any interference of native barium which vitiates results obtained by the generally followed hydrochloric acid extraction. Necessity for silica dehydration is obviated and a minimum of potassium salts is insured.*

occlusion of sulfate in the hydrated ferric oxide.

Hart and Peterson<sup>6</sup> compared the official (Hilgard), modified Van Bemmelen aqua regia, and Osborne sodium peroxide methods. They concluded that the latter was superior, even without elimination of ferric and aluminium chlorides

and silica from solution prior to precipitation of barium sulfate. The Osborne<sup>14</sup> method, applied to soils, calls for the solution of the sodium hydroxide-peroxide melt with hydrochloric acid, and addition of an indefinite amount of ammonia to neutrality. The original Fraps<sup>5</sup> method using potassium nitrate ignition after a preliminary digestion with nitric acid, and its subsequent modification<sup>9</sup> calling for calcium nitrate instead of potassium nitrate when applied to soils, both called for hydrochloric acid solution of ignited residue. Hart and Peterson<sup>6</sup> made a hydrochloric acid solution of the peroxide melt without elimination of iron and at a volume sufficient to inhibit precipitation of silica. Shedd<sup>15</sup> also obtained a strong hydrochloric acid solution of the peroxide melt, leaving iron and silica in the solution and guarding against inclusion of silica in the barium sulfate by hydrofluoric plus sulfuric acid ignition. In the A. O. A. C. official method<sup>2</sup> the 1-gram soil-charge fusion with 5 grams of sodium carbonate is extracted with hydrochloric acid and made to volume, 0.2 or 0.4-gram equivalent aliquots being used for the determination of barium sulfate. In using magnesium nitrate to effect oxidation, Swanson and Latshaw<sup>16</sup> made a hydrochloric acid solution of the pulverized, ignited residue.

In all the foregoing it will be observed that the melt was dissolved in hydrochloric acid. This the authors believe to be a serious disadvantage, if not an error, for several reasons: first, the excess of acid necessary to effect solution is stronger than permissible for the precipitation of barium sulfate; secondly, native barium and strontium present as carbonates are dissolved and during the prescribed digestion some barium sulfate is occluded in the acid-insoluble portion of the melt; thirdly, the interfering elements iron, aluminium, and possibly manganese are dissolved; and fourthly, the alkali and alkali-earth silicates are dissolved and maximum silica content is carried by the hydrochloric acid solution. In the procedure advanced by the writers, the melt is disintegrated by aqueous digestion and filtered before acidifying. By this process all iron, barium, and some aluminium are retained as silicates or carbonates in the water-insoluble residue, while much of the silica is eliminated as silicates.

In only the Hillebrand<sup>7</sup> method, where potassium nitrate is used, does it appear that the melt is dissolved in water and filtered from alkaline solution. Practically the identical technic used by Hillebrand has been advanced recently by Thomas,<sup>18</sup> and by Mahin and Carr.<sup>13</sup> In the present method the minimum of undesirable potassium salts is insured and the advantageous features of several different procedures have been incorporated.

<sup>1</sup> Received August 20, 1923.

\* Numbers in text refer to bibliography at end of article.

## PROCEDURE

The instructions and notes sent out to A. O. A. C. collaborators are here given.

**PREPARATION OF MIXTURE**—Place a 5 to 10-gram charge of 0.5-mm. fineness into a 100-cc. nickel crucible; add equal weight of C. P. anhydrous sodium carbonate, and mix well with a stout nickel stirring rod of such length as to permit introduction into the furnace to be used in the fusion. Pipet carefully 4 cc. of water into each 10 grams of soil; stir well to a stiff paste, adding more water if necessary, a few drops at a time. Immediately add successive portions of about 1 gram of sulfur-free sodium peroxide, stirring well after each addition to obviate excessive frothing and overflow. Continue to add peroxide until the mixture becomes dry and granular, and then add, as a surface coating, enough to make the total peroxide addition 25 grams per each 10 grams of soil. Place the mixture in an electric furnace.

**FUSION OF MIXTURE**—Maintain a temperature of between 400° and 500° C. during the first half hour, then raise the temperature rapidly to bright red heat (about 900° C.) and continue the fusion at this temperature for about 10 minutes. Withdraw the crucible from the muffle quickly, manipulate so as to cause the melt to spread out in a thin sheet over the interior of the crucible, and cool rapidly by contact with some good conductor in cool atmosphere.

**DISINTEGRATION OF MELT**—Place the chilled crucible sideways in 600-cc. beaker; immerse in distilled water. Add about 5 cc. of ethyl alcohol to decompose sodium manganate. Cover beaker with watch glass, place on a cold electric hot plate, and apply heat. Boil briskly until all the melt is disintegrated (30 minutes are ordinarily sufficient). When the suspension has assumed a flesh-colored, flocculent appearance, with no glassy green lumps of the melt in the interior of the crucible, remove the crucible and rod from the beaker and wash any flaky particles back into beaker with the aid of a policeman, rinsing several times with hot water. (Should small glassy particles still cling to the inside of the crucible, disintegrate by boiling water in the crucible over the hot plate or a small flame and add crucible content to main volume.) Filter immediately by suction through a 9-cm. Büchner—a liter beaker placed under a bell jar being the most convenient arrangement.

**FILTRATION AND WASHING**—When no more of the liquid can be drawn through the filter, return residue together with the filter paper to the original beaker, washing any adhering particles carefully from the funnel. Add about 1 gram of sodium carbonate, macerate with the stirring rod, add 75 to 100 cc. of water, and bring to a brisk boil while *stirring vigorously*. Again throw on to a Büchner filter, suck nearly dry and wash three or four times, with about 20 cc. of hot water, to a volume of 500 cc., or 700 cc., for the 5 and 10-gram charges, respectively.

**ACIDULATION OF FILTRATE AND DEHYDRATION OF SILICA**—Cover the beaker containing the filtrate with a watch glass and (*important*) place a supported funnel with its stem bent so it just reaches into the lip of the beaker. Through the funnel pour gradually about 80 cc. of concentrated hydrochloric acid per each 10-gram charge of soil, taking care that the acid runs down the side of the beaker. Slightly lift the cover glass and gently stir with a stirring rod, watching for strong effervescence. If effervescence does not ensue, add more acid *immediately* until effervescence occurs. *If the filtrate remains clear* when concentrated to a volume of 400 cc., the barium sulfate precipitation may be effected immediately by the addition of barium chloride solution, with the silica remaining in solution.<sup>7</sup>

However, to cover all cases, proceed as follows: Transfer acidulated filtrate to a shallow porcelain evaporating dish of 1000-cc. capacity as soon as effervescence has ceased. Place the dish 1 to 2 inches above an electric hot plate at full heat. When crystallization begins, raise the dish about 3 inches from the hot plate. Permit evaporation and dehydration without stirring, breaking the surface crust occasionally to expedite evaporation.

**PRECIPITATION OF BARIUM SULFATE**—To the dehydrated mass add 0.5 cc. hydrochloric acid and 200 cc. water. Dissolve the salts completely by warming. Filter off the silica on a Hirsch funnel using No. 2 Whatman filter, or paper of equivalent texture. Wash six times with hot water to a volume of about 400 cc. Heat the filtrate, add slowly 10 cc. of 5 per cent barium chloride solution, and allow to stand over night. Filter barium sulfate on a Gooch asbestos filter, ignite in an electric furnace (or place Gooch in a porcelain crucible over a burner flame), cool, and weigh.

## NOTES AND SUGGESTIONS

**FUSION MIXTURE**—Sodium carbonate serves both to moderate the speed of the oxidative process and to eliminate barium as barium carbonate in the first extraction. Optimum proportions of charge and sodium carbonate have been determined empirically by means of charges of pure quartz. The addition of sodium peroxide should be so regulated as to permit the comfortable handling of the crucible with the fingers, which will obviate excessive frothing and loss from overflow. Time is conserved by the simultaneous mixing of a number of charges. Should solidification of the mixture occur at any time during the mixing process, it may be reverted to the pasty consistency by immersion of crucible into hot water for a few minutes.

**FUSION OF MIXTURE**—Speed is insured by the use of a large electric furnace, but any sulfur-free heat may be utilized. It is important that the specified temperature be not exceeded until the preliminary oxidation process has been insured, after which complete disintegration should be effected at a higher temperature. The formation of a thin layer of the melt and its rapid crystallization on the interior of the crucible are essential to maximum efficiency.

**DISINTEGRATION OF MELT**—The melt is usually completely disintegrated by the procedure outlined. Aqueous digestion over night offers no advantage. Furthermore, the successful use of the hot plate is conditioned upon the fact that the disintegration is started with a clear liquid in the beaker and with all the melt contained in the crucible. The presence of suspended material in the beaker at the beginning will make the use of the hot plate impossible on account of severe bumping, and a steam bath or water bath will have to be employed with a consequent delay of 2 or 3 hours in the process. The disintegration is completed by the action of the boiling water alone without any other mechanical agitation.

**FILTRATION AND WASHING**—The filtration of the alkaline aqueous extract removes iron, manganese, a good portion of the aluminium, all the barium, and earthy bases—mostly in the form of carbonates and silicates.

**ACIDULATION OF FILTRATE AND DEHYDRATION OF SILICA**—The covering of the beaker and addition of acid as directed, rather than pouring in and stirring with a rod, is most important. *Often no silica precipitation takes place*, particularly if the solution is left to come to room temperature prior to addition of acid, even after subsequent concentration to a volume far below that from which the barium sulfate precipitation is made. By this procedure the dehydration process is also greatly facilitated and expedited. The silica usually comes out as coarse crystals after some sodium chloride has crystallized and the full evaporation and dehydration is accomplished in about 4 hours. The use of inverted tripods on the hot plate affords a very convenient means of adjusting the distances for the evaporation and dehydration of the silicic acid.

Barium chloride additions show no detrimental effect upon sulfate recoveries and sulfates added to the melt as barium sulfate are completely recovered.

## EXPERIMENTAL

Since a perfectly clear melt is obtained by the fusion technique, it is apparent that complete disintegration of the soil

TABLE I—EFFECT OF SOLUBLE AND INSOLUBLE SULFATE ADDITIONS TO SOILS UPON THE SULFATE RECOVERY OBTAINED BY THE PROPOSED METHOD

SOIL	Weight of Sample G.	BaSO <sub>4</sub> Equivalent of Addition as		BaSO <sub>4</sub> Determined			Recovery of BaSO <sub>4</sub> Equivalent of Sulfate Addition	
		FeSO <sub>4</sub> G.	BaSO <sub>4</sub> G.	A G.	B G.	Average G.	Actual G.	Variation G.
Tennessee 4893	5	None	None	0.0115	0.0125	0.0120		
Tennessee 4893	10	0.1851	None	0.2101	0.2085	0.2093	0.1853	0.0002
Kansas 1	5	None	None	0.0224	0.0222	0.0223		
Kansas 1	5	0.0755	None	0.0980	0.0992	0.0986	0.0763	0.0008
Kansas 1	5	None	0.1000	0.1217	0.1225	0.1221	0.0998	-0.0002

mass is assured. It is next essential (1) that complete removal of sulfate be secured, and (2) that barium, and possibly strontium, exert no interference in the removal of sulfates formed during the oxidative and disintegrative reactions utilized in obtaining a perfect melt. Since all barium and strontium are converted into carbonate form and a large excess of carbonate is present in the aqueous solution of the melt, those elements may be considered as eliminated as silicates along with iron and aluminium by the proposed procedure. To assure attainment of these two essentials, two soils, one from Tennessee and one from Kansas, were fortified with soluble and insoluble sulfates. The use of barium sulfate for the latter purpose provides both an insoluble sulfate and the presence of the interfering element barium. Full recoveries of both added soluble and insoluble sulfates are shown by the data of Table I, which gives the differences between the two soils before and after fortification.

The further fact that the presence of either soluble or insoluble barium in the soil before sodium carbonate-peroxide fusion is of no effect upon the recovery of sulfate, is also shown by the data of Table II.

TABLE II—EFFECT OF SOLUBLE AND INSOLUBLE BARIUM ADDITIONS TO SOIL UPON SULFATE RECOVERY BY THE PROPOSED METHOD<sup>a</sup>

BaSO <sub>4</sub> Equivalent of Additions of Barium as		BaSO <sub>4</sub> Determined			Variation in BaSO <sub>4</sub> Equivalent Recovery as Influenced by Barium Additions <sup>b</sup>
BaCl <sub>2</sub> G.	BaSO <sub>4</sub> G.	A G.	B G.	Average G.	G.
None	None	0.0224	0.0222	0.0223	.....
0.0250	None	0.0230	0.0211	0.0221	-0.0002
None	0.1000	0.1217	0.1225	0.1221	-0.0002

<sup>a</sup> A 5-gram sample of Kansas 1 soil was used in each determination.  
<sup>b</sup> BaCl<sub>2</sub> and BaSO<sub>4</sub> additions may be considered as additions of BaCO<sub>3</sub> and BaCO<sub>3</sub> plus Na<sub>2</sub>SO<sub>4</sub>, since the Na<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>O<sub>2</sub> fusion converts all barium to the carbonate form in the melt.

The removal of iron and aluminium in granular form by an aqueous extraction and filtration of the melt is very desirable. The primary consideration in mind, however, was that of elimination of the barium, for the hydrochloric acid solution of the melt brings into play the undesirable preliminary reaction of soluble barium chloride and soluble

itated from a hydrochloric acid solution of the melt, without the removal of silica by dehydration, an excess of acid exerts a solvent action upon the barium sulfate formed after the addition of the barium chloride solution. Again, this excess of hydrochloric acid may not be killed off by ammonia, because of (1) the undesirability of ammonium salts, (2) the necessity for an absolute blank upon the amount of ammonia used, and (3) the necessity for sufficient excess of acid to care for the dissolved iron, aluminium, and manganese. As stated previously, the aqueous extract has additional advantages over the acid solution of the melt. The insoluble residue from the melt not only removes all barium, strontium, iron, manganese, and phosphorus pentoxide, but it leaves these elements for separate determination. In addition, it takes from solution more silica than does the acid solution.

The recoveries of sulfate by aqueous and hydrochloric acid extractions for soil and soil fortified with barium chloride and barium sulfate are shown by the data of Table III. It is apparent that the recovery of sulfate by the acid extraction is consistently lower than that obtained in the aqueous alkaline extraction. It is also apparent that a constant of sulfate and an increase in barium result in an increased discrepancy between the two methods of extraction. It is still further emphasized that, with high sulfur content, sulfate unrecovered by the acid extraction is practically equivalent to the amount added. But in the aqueous extraction of the fortified soil the recovery was equivalent to the amount of insoluble sulfate added. These data demonstrate the fallacy of hydrochloric acid extraction of soil melts; this point has not been stressed by investigators, so far as the writers are aware. The data of this table afford further proof that normal and abnormal occurrences of barium are of no effect in hindering sulfate recovery from soil melts.

Variations between 5 and 10-gram charges had no effect upon the accuracy of the method. In comparisons between these two charges it was found that the proportionate recoveries were obtained with a constant ratio of soil to sodium carbonate-peroxide. Comparisons are therefore absolute when the results from the more feasible 5-gram charges of

TABLE III—COMPARISON BETWEEN AQUEOUS AND HYDROCHLORIC ACID SOLUTIONS OF MELTS OF SOIL AND SOIL FORTIFIED WITH BARIUM CHLORIDE AND BARIUM SULFATE

SOIL <sup>a</sup>	BaSO <sub>4</sub> Equivalent of Barium Addition as		BaSO <sub>4</sub> DETERMINED			HCl Extraction			Variation between Acid Extract and Aqueous Alkaline Extract G.
	BaCl <sub>2</sub> G.	BaSO <sub>4</sub> G.	Aqueous Alkaline Extraction		Average G.	A G.	B G.	Average G.	
	A G.	B G.	A G.	B G.					
Kansas 4	None	None	0.0182	0.0200	0.0191	0.0154	0.0170	0.0162	-0.0029
Kansas 5	None	None	0.0180	0.0185	0.0183	0.0124	0.0140	0.0132	-0.0051
Kansas 6	None	None	0.0130	0.0124	0.0127	0.0107	0.0102	0.0104	-0.0023
Kansas 1	None	None	0.0224	0.0222	0.0223	0.0140	0.0130	0.0135	-0.0086
Kansas 1	0.0250	None	0.0211	0.0230	0.0221	0.0224	0.0285	0.0254	-0.0967
Kansas 1	None	0.1000	0.1225	0.1217	0.1221				

<sup>a</sup> A 5-gram sample used.

sulfate. With increased concentration of the hydrochloric acid solution of the melt this reaction between native barium and sulfur may be minimized during the preliminary digestion prior to filtration. However, if the hydrochloric acid extract is evaporated to effect removal of silica, as prescribed in most of the acid extractions of melt, still further opportunity is afforded for barium sulfate precipitation and loss along with the dehydrated silica. Or, if the barium sulfate is precip-

itated from a hydrochloric acid solution of the melt, without the removal of silica by dehydration, an excess of acid exerts a solvent action upon the barium sulfate formed after the addition of the barium chloride solution. Again, this excess of hydrochloric acid may not be killed off by ammonia, because of (1) the undesirability of ammonium salts, (2) the necessity for an absolute blank upon the amount of ammonia used, and (3) the necessity for sufficient excess of acid to care for the dissolved iron, aluminium, and manganese. As stated previously, the aqueous extract has additional advantages over the acid solution of the melt. The insoluble residue from the melt not only removes all barium, strontium, iron, manganese, and phosphorus pentoxide, but it leaves these elements for separate determination. In addition, it takes from solution more silica than does the acid solution.

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## Determination of Dissolved Oxygen in the Presence of Iron Salts<sup>1</sup>

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THE determination of dissolved oxygen is undoubtedly the most frequently used and the most important of all the chemical methods available for the investigation of water pollution problems. It measures the capacity

of a body of water for receiving organic matter without causing nuisance; it measures one of the important factors affecting fish life; it is one of the important steps in the biological oxygen demand test for measuring the important portion of the oxidizable substances in the sample; and it furnishes valuable information concerning the biological and biochemical reactions going on in the stream. Naturally, a determination of such importance has received considerable attention in the past—in fact, no less than thirteen distinct methods have been proposed.

To be successful, a method for determining dissolved oxygen must meet two requirements. First, on account of the small amount of substance to be determined (a few milligrams per liter), it must be exact; second, it must be carried out in compact, light apparatus capable of field operation, since the samples cannot be transported without undergoing chemical change.

### PREVIOUS WORK

The method least subject to chemical errors and probably the first to be proposed is that of Bunsen.<sup>1\*</sup> In this method the gases are boiled out either under atmospheric pressures or diminished pressures as practiced by Adeny,<sup>2</sup> Thresh,<sup>3</sup> and others.<sup>4</sup> The gas collected is then determined by ordinary absorption methods. It is too cumbersome for field work (although Birge<sup>5</sup> has designed a metal apparatus for field use) and requires considerable skill for accurate manipulation, but it is still the standard by which all new volumetric or colorimetric methods are judged.

Shutzenberger<sup>6</sup> made use of the absorption of oxygen by sodium hyposulfite. The determination was made in a current of hydrogen with indigo as an indicator. The hyposulfite solution was standardized against an ammoniacal copper sulfate solution. Investigators differed on the reliability of this method. It was claimed that hydrogen peroxide was formed during the titration and the results were said to be too low, with variations of 0.5 cc. from gasometric methods.

Mohr<sup>7</sup> made use of the oxidation of ferrous iron to ferric iron by the dissolved oxygen in an alkaline solution. To

*A review of the literature on the determination of dissolved oxygen is given. The modified Winkler method is shown to give erroneous results in the presence of iron salts. These errors cannot be corrected by applying a factor based on the amount of iron present. The Letts and Blake modification of the Levy method is found to give results which check the gasometric determinations in the presence of iron salts and organic matter.*

one of duplicate samples he added a solution of standard ferrous iron, made the water alkaline with ammonium hydroxide and then acid; to the other he added acid immediately, then standard ferrous solution, and titrated both with standard permanganate. The difference between the two titrations is

proportional to the amount of oxygen in the water. Some investigators have declared that this method gives low results, while others say the results are too high.

Levy<sup>8</sup> modified Mohr's method using potassium hydroxide and a bulb with a stopcock at both ends and a funnel at one end to introduce the reagents. Letts and Blake<sup>9</sup> used a separatory funnel and sodium carbonate as the alkali.

Thresh's<sup>3</sup> method consists in the oxidation of hydriodic acid by the oxygen in the water to give free iodine. This is done in the presence of nitrites, which by forming nitric oxide furnish a carrier for the oxygen. A blank is run to correct for the nitrite added and that present in the water. The released iodine is titrated with standard thiosulfate in a current of coal gas or under a layer of petroleum. This method is accurate but too cumbersome for field use.

Direct titration of the dissolved oxygen was accomplished by Linoissier.<sup>10</sup> He avoided precipitation of iron by the presence of sodium potassium tartrate and titrated the free oxygen with standard ferrous sulfate solution with phenolsafranin as an indicator.

A few colorimetric methods have been proposed. Ramsay<sup>11</sup> allowed the oxygen in the water to oxidize a cuprous salt to a cupric salt, thus going from a colorless to a blue solution. The intensity of the color was proportional to the oxygen present. He used standard tubes made from sodium chloride and copper sulfate reduced with sulfur dioxide gas as comparates. His method was never successful, since the color faded from the standards on standing, and the color of the water interfered as also did the nitrites. Mackay and Middleton<sup>12</sup> absorbed the oxygen from a portion with alkaline pyrogallol. They boiled another equal portion to get rid of the oxygen and after the addition of pyrogallol to the boiled sample added air until the color matched the first sample. From the amount of air added the dissolved oxygen was calculated. The method was inaccurate because the air added could not be easily measured and the apparatus required was cumbersome.

The method commonly used at present for the determination of dissolved oxygen in water is that of Winkler.<sup>13</sup> It depends on the oxidation of bivalent manganese ( $Mn^{++}$ ) by the dissolved oxygen in an alkaline solution. The oxidized manganese oxidizes iodide in an acid solution, giving free iodine. The liberated iodine is titrated with standard sodium thiosulfate solution. This method has been found to check very well with gasometric determinations. It gives too high results in the presence of nitrites. Winkler<sup>13</sup> recognized this fact and proposed to correct by titrating a separate sample with a weak manganese chloride solution. This means is out of the question for field work.

<sup>1</sup> Presented before the Division of Water, Sewage, and Sanitation at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

\* Numbers in the text refer to the bibliography at end of the article.

The modification now adopted by the Standard Methods of the American Public Health Association is that of Rideal and Stewart,<sup>14</sup> which oxidizes the nitrites and easily oxidizable matter in the water with potassium permanganate in acid solution. The excess permanganate is subsequently destroyed with sodium oxalate. Hale and Melia<sup>15</sup> have prevented the effect of nitrites by adding potassium acetate before titration, thus repressing the hydrogen-ion concentration and preventing the interaction of the nitrites with the hydrogen iodide.

Winkler<sup>16</sup> has recently proposed a method for the estimation of dissolved oxygen in the presence of much nitrate and organic matter. He oxidizes the organic matter with hypochlorite. One sample is run as a blank and another after treatment with manganese chloride, potassium hydroxide, and potassium iodide, the same as in his original method.

While a relatively large amount of work<sup>17</sup> has been done in correcting the Winkler method for nitrites and organic matter, no attention appears to have been given to the possibility of interference from other sources. Iron salts, for example, would be expected to interfere with an iodometric titration. Whether this interference is quantitative, and hence possible of correction by calculation, is not apparent from the literature.

The authors had met with the interference of iron salts in attempting to determine the dissolved oxygen in a stream polluted with waste liquor from a galvanizing plant as well as domestic sewage. Since no solution of the difficulty was found in the literature the question was submitted to the following investigation:

#### EXPERIMENTAL

A series of glass-stoppered bottles containing distilled water, potassium iodide, acid, and iron salts was set up. The amounts of iron in the respective bottles varied from 0 to 170 p. p. m., as shown in the table. They were allowed to stand and then titrated with standard thiosulfate solution. The results are shown in Table I.

TABLE I

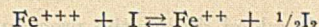
In all cases 4 cc. concentrated HCl, 450 cc. distilled water, and 10 cc. KI solution (1 cc. = 0.03994 gram KI) were used, together with indicated amount of iron solution (1 cc. = 0.0100294 gram iron); shaken, allowed to stand 12 hours, and titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.01317 N)

No.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Solution for 100 Cc.		Iron in Original Solution P. p. M.	Iron Reduced		Apparent Dissolved Oxygen P. p. M.
	Iron Solution (Av. of 2 Titrations) Cc.	Water for Bottle Cc.		P. p. M.	Per cent	
1	0	0.00	0.00	0.0	0.0	0.0
2	1	0.30	1.40	20.2	93.5	2.89
3	2	0.70	3.27	40.3	93.7	5.77
4	4	1.36	6.38	74.1	86.5	10.58
5	5	1.99	9.38	92.4	86.4	13.20
6	7	2.55	12.09	120.8	80.8	17.25
7	8	2.55	12.09	131.9	77.6	18.85

Since many unpolluted waters contain appreciable amounts of iron but seldom as much as 20 p. p. m., the smallest amount used in the first series, another series was run with smaller amounts varying the iron from 0 to 20 p. p. m., in order that the entire range of probable conditions might be covered. These results are shown in Table II.

That iron affects the determination of dissolved oxygen by the Winkler method is apparent from the foregoing data. This effect may be brought about in two ways. First, when present in large amounts it requires so much of even strong potassium permanganate to oxidize it from the ferrous to ferric condition that the dissolved oxygen in the reagent itself is appreciable; second, when oxidized to the ferric state it serves as an oxidizing agent itself and will oxidize the iodide ion to free iodine which will give high results.

The chief objection to the use of the Winkler method when iron is present is due to the second effect. If all the iron present were reduced and the amount of iron present were known, it would be possible to correct the titration with thiosulfate. If, however, the reaction



does not go to completion, then the correction will not equal the amount of iron present. From the tables it will be seen that as the amount of iron increases a smaller percentage of the iron is reduced (seventh column). This means then that if we were to apply a correction in the Winkler method when iron is present, we should know not only the iron content, but also the percentage which acts on the iodide solution forming free iodine. Such a percentage value would vary with the temperature and foreign substances present, as well as with iron, hydrogen-ion, and iodide-ion concentration in solution. Table II shows that at a concentration of 2 p. p. m. all the iron in solution is reduced and the reading on titration with thiosulfate will be increased directly as the amount of iron present.

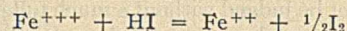
TABLE II

In all cases 4 cc. concentrated HCl, 450 cc. distilled water, and 10 cc. KI solution (1 cc. = 0.03994 gram KI) were used, together with indicated amount of iron solution (1 cc. = 0.001003 gram iron); shaken, allowed to stand 12 hours, and titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.01308 N)

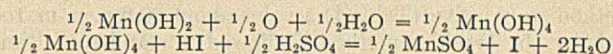
No.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Solution for 100 Cc.		Iron in Original Solution P. p. M.	Iron Reduced		Apparent Dissolved Oxygen P. p. M.
	Iron Solution (Av. of 2 Titrations) Cc.	Water for Bottle Cc.		P. p. M.	Per cent	
1	0	0.00	0.00	0.00	0.0	0.00
2	1	0.30	1.40	2.16	2.20	100 <sup>a</sup> 0.31
3	2	0.70	3.27	5.38	5.13	95.4 0.73
4	4	1.36	6.38	10.69	9.96	93.2 1.42
5	5	1.99	9.38	15.95	14.57	91.3 2.08
6	10	2.55	12.09	21.16	18.68	88.3 2.67
Tap water		0.49	...	About 2	...	.. 0.51

<sup>a</sup> Excess 0.04 p. p. m. reduced iron over actual iron in solution is within titration error.

Ferric iron on being reduced to the ferrous condition releases one equivalent of iodine per atom of iron.



Oxygen, on reacting with manganese hydroxide forming the higher hydroxide which subsequently reacts with the iodide solution, releases one equivalent of iodine per one-half atom of oxygen.

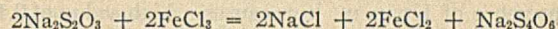


Therefore, one atom of iron equals one-half atom of oxygen, or 56 grams Fe = 8 grams O.

$$8/56 \times \text{grams Fe} = \text{grams O}_2$$

The presence of one part per million of iron would indicate 0.14 p. p. m. dissolved oxygen more than is actually present. Since only about 90 per cent of the iron is converted the correction would be a little lower. Although in most cases this correction is smaller than the error in titration in the field, when the amount of iron is high as in the discharge from iron and steel works, it amounts to an appreciable error.

There is another way in which iron affects the Winkler method. The thiosulfate may react with the ferric iron itself directly according to the equation:



However, most of the ferric iron has been reduced before this titration is made, so the error due to this cause is rather small, especially in low iron-bearing waters. From the equation it is seen that the error in the titration will be the same as if that amount of iodine is actually present, since the reaction is almost complete to the right.

Since the Winkler method apparently could not be modified for use in the presence of iron, the next step was to investigate some other method.

Of those mentioned above the Levy-Mohr<sup>8</sup> method seemed to be the one most likely to work in the presence of iron, since

an iron solution is added during the procedure and therefore any iron already in the water should have no effect.

As to the accuracy of the Levy method and its modifications there is considerable difference of opinion. The Metropolitan Sewage Commission of New York<sup>18</sup> has used it and found close agreement with gasometric methods. Letts and Blake<sup>9</sup> claim high results in the presence of nitrites or organic matter, while others, such as Chlopin,<sup>19</sup> and Tiemann and Preusse,<sup>20</sup> maintain that it gives low results, the magnitude of the error depending on the amount of time allowed for the precipitate to stand, the degree of pollution of the water and the temperature at which the experiment is run. The longer the precipitate is allowed to stand before acidification the less the error. Waters run at higher temperature have given higher results than some run at a lower temperature, which is contrary to the law of solubility of gases.

With the end in view of seeing how variable amounts of iron affected the Levy method, a series of runs was made varying the amount of iron both in distilled and polluted water. The samples were tested by the Levy method, Letts and Blake modification, and also by gasometric methods.<sup>21</sup> The results are shown in Table III.

TABLE III—COMPARISON OF LEVY AND BOILING OUT METHODS

No.	Iron		Boiling		Boiling <sup>a</sup>		REMARKS
	P. p. M.	P. p. M.	P. p. M.	P. p. M.	Cc.	Cc.	
Distilled Water							
1	107	7.70	7.68	5.39	5.38		
2	81	7.35	7.65	5.15	5.35		
3	54	7.56	7.36	5.26	5.15		
Raw Sewage							
4	81	0.77	0.86	0.54	0.60	(Shaken with iron solution and allowed to stand for a few hours)	
5	54	0.35	0.43	0.25	0.30		
6	27	0.28	0.22	0.20	0.15		

<sup>a</sup> At normal temperature and pressure.

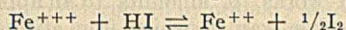
There is in general a close agreement in the results by the two methods. Whether or not the criticisms of this method are false cannot be judged without a much fuller investigation. The data, however, show that the Levy method can be used in the presence of iron and will give far more accuracy than the Winkler method, Rideal and Stewart modification. For instance, a water containing 107 p. p. m. (Table III) which gives a correct value for the dissolved oxygen by the Levy method would give (Table I) a value about 10.6 p. p. m. too high by the Winkler method if allowed to stand some time before titration with thiosulfate.

Another phase of the problem to be studied in this laboratory is the effect of time on the equilibrium of iron and hydrogen iodide. It is thought that it plays a considerable part.

#### CONCLUSION

Determination of dissolved oxygen with the Winkler method, Rideal and Stewart modification, gives high results in the presence of iron.

A correction cannot be made for iron by lowering the results in proportion to the iron present. The equilibrium



must be considered.

Reaction gives 75 to 90 per cent of iron as iodine. Thus, the presence of 1 p. p. m. iron causes a high value of 0.10 to 0.13 p. p. m. in the oxygen.

The Levy method gives accurate results in the presence of iron and organic matter, while the Winkler method gives too high results.

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## Fractional Distillation Apparatus<sup>1</sup>

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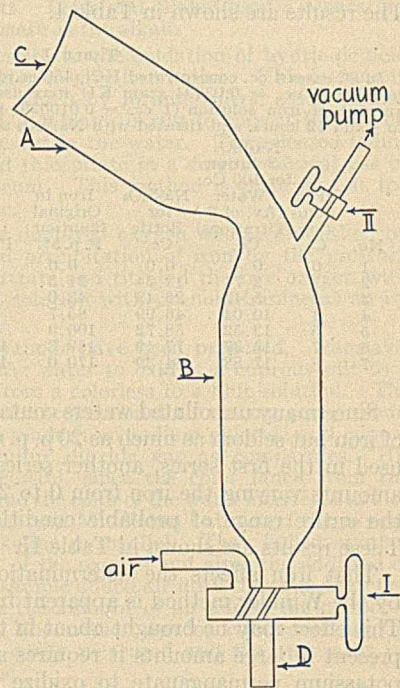
THE types of apparatus used for fractional distillation under diminished pressure, such as bird cages and other varieties designed by Kolbe, Wechmar, Gautier, and others,<sup>2</sup> are expensive, very inconvenient when large quantities of distillate are to be obtained, and often fragile. The following apparatus, which is merely a modification of that used by Fischer and Harries,<sup>3</sup> has several advantages. It is very inexpensive, easy to manipulate, is not fragile, and with it distillates of any size may be obtained.

As shown by the diagram, the apparatus may be made with an adapter, A, a pipet, B, and two stopcocks, I and II. The adapter is connected with the condenser at C and the receiver, which may be of any size depending upon the quantity of distillate, is attached at D. The apparatus is connected to a vacuum pump at stopcock II. After the first fraction is obtained, stopcock I is turned to admit air into the receiver. During the exchange of receivers, the distillation may be continued, the distillate collecting in the pipet. Distillation will only momentarily stop while the second receiver is being evacuated. When heavy liquids are to be distilled, it is well to have the bore of stopcock I, which leads to the receiver, of good size.

<sup>1</sup> Received May 17, 1923.

<sup>2</sup> Houben-Weyl, "Die Methoden der organischen Chemie," Vol. 1, 2nd ed., p. 567.

<sup>3</sup> *Ber.*, 35, 2158 (1902).





# Correlation of High School and College Chemistry

## Preliminary Report of the Committee on Chemical Education of the American Chemical Society

**T**HE Committee on Chemical Education of the AMERICAN CHEMICAL SOCIETY which has been charged, during the past year, with correlating courses of high school and college chemistry, had its first official session at New Haven at the spring meeting of the SOCIETY. The committee decided that the four following objectives would help most in solving the correlation problem:

- 1—To encourage the teaching of chemistry in the high school.
- 2—To have such a course given in high school that it would answer for students who go to college as well as for students who do not go to college.
- 3—To outline a minimum high school chemistry course, taking into account both content and method.
- 4—To have colleges recognize high school chemistry, at least to the degree of having a different course for those students who have had the said outlined high school course.

These four points were taken before the Section of Chemical Education and after some discussion were approved, and hence the committee began to make plans for their development. The most direct point of contact was the preparation of the high school outline which the committee has termed "A Standard Minimum High School Course in Chemistry."

The following objectives have governed the committee in its work:

- 1—To prepare an outline for high school chemistry which is satisfactory for students who wish to get a general knowledge of chemistry as well as for those who are going to college.
- 2—To list only the minimum essential topics which are common to all localities, so that the high school teacher will have time in developing the course to supplement these minimum topics with material which he considers especially suitable for his locality or for the future work of his students. See list of topics for supplementary work at end of this report.
- 3—To prepare an outline which would cover the essentials of any State requirements.
- 4—To prepare an outline which would be in tune with the syllabus of the College Entrance Examination Board.

It is the anticipation of the committee that the following objectives will govern the high school teacher in developing the outline:

- 1—To show the service of chemistry to the home, to health, to medicine, to agriculture, to industry, etc.—in a word, to show the service of chemistry to the Nation.
- 2—To develop this service in chemistry around these minimum standard topics, and, in doing so, to see that these minimum requirements are so well taught that they may be built upon as a foundation in college.
- 3—To use his own order of developing the listed topics.
- 4—To train the student in keen observation and exact reasoning.
- 5—To develop a careful correlation between recitation and experiment with the minimum amount of repetition.
- 6—To encourage students to keep notebooks which shall be an accurate record of laboratory experiences expressed in concise, clear English.
- 7—To encourage chemistry being placed in fourth year of high school after the students have had a year of general science, and a year of biological science or physics, or preferably both.
- 8—To build upon the earlier science courses and knit them together in the best possible manner.
- 9—To encourage students to use reference books in addition to their textbook.
- 10—To help pupils to find themselves—i. e., to discover whether they have an aptitude for further study in chemistry or applied science, and, if so, to encourage such students to continue their study of science in university or technical school.
- 11—The teacher is urged throughout the course to stress the general principles involved in the specific cases studied.

### TOPICS FOR A STANDARD MINIMUM HIGH SCHOOL COURSE IN CHEMISTRY

- 1—Water
  - (a) General distribution
  - (b) Physical properties: color, odor, taste, density, boiling point, freezing point
  - (c) Solution: solvent, solute, saturated solution, process of solution, degrees of solubility, factors affecting the solubility of a substance, suspensions
  - (d) Impurities in water: what constitutes impurities; purification by boiling, distillation or filtration
  - (e) Crystallization: water vapor, water of hydration, deliquescence and efflorescence
  - (f) Chemical properties: quantitative composition of water by electrolysis and by synthesis from copper oxide, contrast of physical and chemical change, contrast of elements and compounds; stability of water; interaction of water with active metals; order of activity; interaction with oxides
- 2—Oxygen
  - (a) Preparation
    - Electrolysis of water
    - Industrial
    - Potassium chlorate (use of catalytic agent)
  - (b) Properties
    - Physical: color, odor, solubility in water, weight relative to air, weight of 22.4 liters
    - Chemical: tendency to form oxides in air and in oxygen, explanation of oxidation and combustion, kindling temperature
  - (c) Uses: necessary to life
  - (d) Ozone, briefly as to its preparation, properties, and uses
- 3—Hydrogen
  - (a) Preparation
    - Electrolysis of water
    - Industrial
    - Action of certain metals—i. e., sodium—on water
    - Replacement in acids by metals
  - (b) Properties
    - Physical: as with oxygen
    - Chemical: burns in air, reduction by hydrogen
  - (c) Uses (practical): oxyhydrogen flame, balloons, hydrogenation of oils
  - (d) Hydrogen peroxide, briefly as to its preparation, properties, and uses
- 4—Laws, Hypotheses, and Theories
  - (a) Law of Conservation of Mass
  - (b) Law of Definite Composition (proportion)
  - (c) Atomic Theory (simple treatment), including electron
  - (d) Law of Boyle and Law of Charles, treated briefly with special reference to gases, not experimentally, but rather their application to the interpretation of change of volume
  - (e) Law of Gay-Lussac and Avogadro's Hypothesis
- 5—Symbols, Weight, and Volume Relations
  - (a) Atomic weights (not their experimental derivative), use in performing simple chemical calculations
  - (b) Molecular weights as explained by Law of Gay-Lussac and Avogadro's hypothesis
  - (c) Symbols and formulas (not their experimental derivative), especially their use in writing equations
  - (d) Valence, with special reference to writing formulas
  - (e) Equations and their use in expressing chemical changes, including gravimetric and volumetric equations
  - (f) Problems involving (1) percentage composition, (2) weights of substance and volume of gases concerned in chemical reactions, and (3) the laws of gases
  - (g) Five kinds of chemical changes: direct combination, decomposition, simple replacement, double replacement, and oxidation and reduction
  - (h) Formulas and writing of equations for reactions already studied
- 6—Air
  - (a) Percentage of oxygen and nitrogen by weight and by volume
  - (b) Test for water vapor and carbon dioxide
  - (c) Liquid air
  - (d) Evidences that air is a mixture and not a compound
- 7—Nitrogen
  - (a) Occurrence
  - (b) Properties
    - Physical
    - Chemical: nonsupporter of combustion, general inactivity, tests

- (c) Nitrogen fixation, as illustrated by plants, synthesis of ammonia, and oxides of nitrogen  
(d) Uses (practical)
- 8—Oxides of Nitrogen**  
(a) Nitric oxide: preparation, properties, tests, and uses  
(b) Nitrogen peroxide: preparation, properties, tests, and uses
- 9—Nitric Acid**  
(a) Preparation  
Industrial (from the air)  
Sodium nitrate with sulfuric acid  
(b) Properties  
Chemical: action of dilute and concentrated nitric acid on copper and silver, test for nitric acid or a nitrate, decomposition products of different nitrates  
(c) Uses: aqua regia, oxidizing agent, nitrocellulose industries, high explosives (briefly)
- 10—Ammonia**  
(a) Preparation  
Decay of nitrogenous matter  
Industrial (Haber process)  
Destructive distillation of soft coal  
Action of ammonium salt with nonvolatile base  
(b) Properties  
Physical  
Chemical: basic character of water solution, ammonium radical formation of ammonium salts, test  
(c) Uses: refrigerating agent, preparation of ammonia water
- 11—Acids, Bases, and Salts**  
(a) Properties  
General: taste, action on litmus, etc.  
(b) Normal and molar solutions  
(c) Activity of acids and bases  
(d) Solutions, conductors of electric current
- 12—Theory of Ionization (briefly)**  
(a) How theory explains electrolysis  
(b) How theory explains neutralization  
(c) Acid and base defined in terms of ions  
(d) Atom and ion distinguished  
(e) Chemical equilibrium  
(f) Reversible reactions  
(g) Why reactions go to completion  
(h) Common ion effect
- 13—Sulfur**  
(a) Occurrence  
(b) Extraction: American method (Frasch method)  
(c) Allotropic forms: rhombic, prismatic, and amorphous, flowers of sulfur  
(d) Properties  
Chemical: direct combination with copper, iron, and zinc  
(e) Comparison with oxygen  
(f) Uses: vulcanizing rubber, making matches, making sulfur dioxide
- 14—Oxides of Sulfur**  
(a) Sulfur dioxide  
Preparation: burning sulfur, roasting of sulfide ores, action of an acid upon a sulfite  
Properties  
Physical  
Chemical: action with water (sulfurous anhydride test)  
Uses: bleaching, reducing agent  
(b) Sulfur trioxide  
Preparation (industrial)  
Catalysis as illustrated by its manufacture  
Properties, including test  
Uses
- 15—Sulfuric Acid**  
(a) Preparation  
Lead chamber process with simple chamber reactions only  
Contact process  
(b) Properties  
Physical: specific gravity and boiling point  
Chemical: affinity for water, dilute acids on metals and concentrated acids on copper, test for  $\text{SO}_4$  ion  
(c) Uses: preparation of other acids, with reason for the same; manufacture of fertilizers; refining of petroleum
- 16—Hydrogen Sulfide**  
(a) Preparation: ferrous sulfide and dilute hydrochloric or sulfuric acid  
(b) Properties  
Physical  
Chemical: combustion, action on metals, action on salt solutions of metallic salts  
(c) Uses: precipitation of sulfides with special reference to testing for certain metals
- 17—Periodic Table for Classification Only**  
(a) Elements arranged in order of atomic weights  
(b) Relation of valence to group numbers  
(c) Gradual transition from metals to nonmetals in passing from Group I to Group II  
(d) Increase of metallic nature with increase of atomic weight within the group
- 18—Halogens**  
A. Chlorine  
(a) Preparation: one industrial method, one laboratory method—oxidation of hydrochloric acid using a chloride and manganese dioxide  
(b) Properties  
Physical  
Chemical: direct combination with other elements to form chlorides, tests, comparison with oxygen  
(c) Uses: bleaching and disinfecting action  
(d) Compound: hydrochloric acid (gas and solution)  
Preparation: a chloride and sulfuric acid  
Properties  
Physical  
Chemical: a typical acid shown by taste, action on litmus, and reaction with metals; test for chloride ion  
Use  
B. Bromine and iodine  
(a) Preparation contrasted with chlorine  
(b) Comparison of physical and chemical properties of chlorine, bromine and iodine; relative replacement; tests  
(c) Uses of iodine  
(d) Position of halogens in the periodic table
- 19—Carbon**  
(a) Occurrence  
General distribution  
Allotropic forms: diamond, graphite, amorphous forms  
(b) Commercial preparation of useful forms: graphite, charcoal, lamp-black, coke, diamond, bone black  
(c) Properties  
Physical  
Chemical: affinity for oxygen, action with calcium and silicon  
(d) Uses: common fuels including carbon or carbon compounds, operation of household stoves and furnaces, reduction by carbon, decolorizer, adsorbent
- 20—Carbon Dioxide**  
(a) Occurrence: relation to plant and animal life  
(b) Preparation: burning carbon or a carbon compound, action of acid on a carbonate  
(c) Properties  
Physical  
Chemical: nonsupporter of combustion, action with soluble hydroxide, brief treatment of its solubility in water, its role in nature, plant growth, temporary hard water, and test for carbonate ion  
(d) Uses: refrigerating, beverages, fire extinguishers, leavening agent in bread-making
- 21—Carbon Monoxide**  
(a) Preparation: from oxalic acid, reduction of carbon dioxide by carbon  
(b) Properties  
Physical  
Chemical: combustibility, reducing power, test  
(c) Uses: reducing agent industrially; constituent of water gas, coal gas, and producer gas  
(d) Illuminating and fuel gases: manufacture and uses
- 22—Sodium**  
(a) Preparation  
Industrial: electrolysis of sodium hydroxide  
(b) Properties  
Physical: metallic luster, hardness, color, power to conduct heat and electricity  
Chemical: flame test; action with water, with chlorine  
(c) Compounds of sodium  
Hydroxide: commercial preparation (either lime soda or electrolytic process); properties as typical base; neutralization; test for hydroxyl ion; use (cleaning agent, soap-making)  
Chloride: occurrence in sea water and mines; laboratory preparation; uses; role in industry  
Carbonate: preparation by Le Blanc and Solvay process; properties; use (particularly industrial)  
Acid carbonate: preparation (laboratory and industrial); properties; uses; baking powders  
Nitrate: occurrence; properties; uses
- 23—Calcium Compounds**  
(a) Carbonate:  
Occurrence: marble, limestone, shells  
Properties: solubility in water containing carbonic acid (temporary hard water), decomposition by heat, action with acids

Industrial uses: building material, making of quicklime, flux in iron furnaces, glass

- (b) Oxide: preparation (industrial); properties; industrial uses  
 (c) Hydroxide: preparation; properties; uses (mortar, its hardening)  
 (d) Sulfate: occurrence; properties; test; uses; permanently hard water and contrast with temporary  
 (e) Bleaching powder: commercial preparation; uses, (bleaching, disinfecting)  
 (f) Calcium phosphates: preparation; uses (fertilizers)  
 (g) Fertilizers: presence of potassium, nitrogen, and phosphorus as ingredients

#### 24—Iron

- (a) Metallurgy (extraction from oxide ores—pig iron—blast furnace)  
 (b) Cast iron: physical properties  
 (c) Uses of cast iron: castings, etc.  
 (d) Steel: manufacture (Bessemer, open hearth, and electrical processes); varieties of iron and steel with reference to their industrial uses  
 (e) Protective coatings to prevent corrosion of iron and steel: tin (tin ware), zinc (galvanized iron), nickel plate, enameled ware, paint  
 (f) Compounds of iron  
 Oxides: occurrence and uses  
 Hydroxide: preparation (laboratory); properties; uses  
 Sulfate: preparation; properties, uses  
 Chlorides (ferrous and ferric): preparation (laboratory); properties; uses; ferrous and ferric compounds; oxidation and reduction of iron compounds; change of valence

#### 25—Zinc

- (a) Metallurgy from carbonate and sulfide  
 (b) Properties  
 Physical  
 Chemical: action with dilute acids, electromotive series  
 (c) Uses: alloys, primary cells

#### 26—Aluminium

- (a) Metallurgy (electrolytic process)  
 (b) Properties  
 Physical  
 Chemical: action with hydrochloric acid and sodium hydroxide, amphoteric  
 (c) Uses: utensils, alloys  
 (d) Compounds  
 Hydroxide: preparation (laboratory); properties; uses; purification of water  
 Sulfate (alum): preparation (laboratory); properties; uses

#### 27—Copper

- (a) Preparation (outline of process only with reference to iron)  
 (b) Purification by electrolysis  
 (c) Electroplating  
 (d) Properties  
 Physical  
 Chemical: action with air and acids  
 (e) Uses: electrical purposes, alloys  
 (f) Compounds of copper  
 Sulfate: properties; uses (water purification, fungicide)

#### 28—Compounds of Lead

- (a) Properties  
 (b) Uses  
 (c) Compounds  
 Lead monoxide: preparation; properties; uses  
 Basic lead carbonate: industrial preparation; properties; uses (paint)

#### 29—Sources of Organic Compounds

- (a) Destructive distillation of wood: methanol, acetic acid, charcoal  
 (b) Destructive distillation of coal: gas, ammonia, benzene, tar, coke  
 (c) Distillation and cracking of petroleum: gasoline, kerosene, vaseline, paraffin

#### 30—Organic Compounds

- (a) Sugar; (b) Starch; (c) Acetic acid (briefly)

#### OPTIONAL LIST

Shall these topics be included? If so, to what extent? Opinions are solicited.

Arsenic	Periodic law
Colloids	Phosphorus
Electrolysis	Rare gases of air
Electronic structure of matter	Reacting weights (not atomic)
Energy change	Silver
Fehling's solution	Zinc chloride
Mercury	Zinc oxide
Other alloys than those contained in copper	Zinc sulfate

#### LIST OF TOPICS FOR SUPPLEMENTARY WORK

- Glass. Crown, flint, lead, special glasses, coloring of glass  
 Clay Products. Brick, pottery, chinaware, porcelain  
 Artificial Stone. Lime, plaster, mortar, hydraulic cement, concrete stucco, plaster of Paris  
 Fertilizers. Problems of soil fertility, elements needed by growing plant and function of each. Photosynthesis and carbon dioxide cycle. Nitrogen cycle and function of nitrogen fertilizers. Use of limestone and phosphate rock  
 Coal. Composition and fuel values of different varieties. Distillation of coal tar, light oil, middle oil, heavy oil, tar, pitch. Relation to dyes and explosives  
 Petroleum. Fractional distillation into burning oils, solvent oils, lubricants, paraffins. Problem of gasoline supply and possible exhaustion of petroleum  
 Wood. Distillation of wood to produce methanol, acetone, acetic acid, charcoal  
 Explosives. Black powder, nitroglycerol, dynamite, guncotton, trinitrotoluene. Relation to nitrogen fixation by arc, Haber, and cyanide processes  
 Paint, Varnish, Etc. Oil paints and driers, varnish, shellac, copal, linseed oil, oil cloth, linoleum  
 Pigments. White lead, red lead, iron oxide, lead chromate, etc.  
 Textile Fibers. Natural and artificial silk. Wool: scouring, bleaching, felting, etc. Cotton: bleaching, mercerizing, etc.  
 Dyeing. Direct and mordant dyes  
 Cleansing Agents. By acid: oxalic, hydrochloric. By alkalis: caustic soda, soap emulsification. By special solvents: carbon tetrachloride, benzene. Composition of trade-marked cleaning fluids  
 Photography. Blueprints, plates, films, prints, toning, etc.  
 Food Constituents. Starch preparations from corn; cooking to dextrin and to paste, hydrolysis to glucose  
 Sugars. Preparation and refining of beet and cane varieties; conversion to caramel; inversion  
 Fats. Olive oil, cottonseed oil, butter, oleomargarine, hardening oils by hydrogenation  
 Proteins. Albumins, casein, gluten, peptones, gelatin, vitamins  
 Beverages. Charged waters, soda, mineral, infusions, tea, coffee, fruit juices (artificial flavors), fermentation  
 Poisons and Common Antidotes. Common inorganic drugs  
 Leavening Agents. Yeast, soda, baking powders  
 Matches. Ordinary and safety types  
 Adhesives. Gums, paste, dextrin, glue, casein, water glass (sodium silicate)  
 Inks. Various types  
 Refuse Disposal. Sewerage, garbage; fermentation and putrefaction; civic problems; disinfectants and deodorizing agents  
 Preserving. Sterilizing, pasteurizing, desiccating, pickling by salt and sugar; chemical preservatives and tests for them  
 Metals. Extraction processes; oxide ore, iron, sulfide ore, lead; electrolysis, sodium and aluminium; extraction of other metals may be studied by comparison with these  
 Metals. Used for basic purposes, iron, copper, aluminium, lead; for ornament, gold, silver, nickel; for alloys, bronze, brass, solder, type metal, antifriction or bearing metals, fusible metal

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The purpose of placing this preliminary report in THIS JOURNAL is to give every chemist an opportunity to criticize it. There will be subcommittees in various sections of the country where arrangements will be made for tabulating such criticisms. If such opportunity is not offered, suggestions may be sent directly to the chairman of the national committee, Neil E. Gordon, University of Maryland, College Park, Md.

NEIL E. GORDON, Chairman	W. D. RICHARDSON
B. S. HOPKINS	R. E. ROSE
J. R. KUEBLER	WALTER SCHMIDT
L. W. MATTERN	W. SCHERBLOM
L. C. NEWELL	R. E. SWAIN

<sup>1</sup> "Reorganization of Science in Secondary Schools," Bureau of Education, Bull. 26 (1920).

At its recent annual meeting, the American Pharmaceutical Association made the following grants for the year 1923-24:

To E. Kremers and K. H. Rang, of the University of Wisconsin, for work on decolorized tincture of iodine and on such other preparations of the National Formulary as time permits—\$250.00.

To W. J. McGill, of the University of Michigan, for work on the electrometric titration of alkaloids—\$200.00.

These research grants are made annually from the interest accruing from the association's research fund, which represents the profits accruing from the sale of the National Formulary.

# The New Patent Act in Canada<sup>1</sup>

By Clayton L. Jenks

120 BROADWAY, NEW YORK, N. Y.

THE Canadian patent law which went into force on September 1, 1923, is so different from the old law that an American inventor or manufacturer may now find it worth while to adopt an entirely new attitude towards the Canadian market.

Heretofore, Canada discriminated against foreigners rather severely. Under the old law, a Canadian patent became void if an article covered by the patent was imported into Canada one year after the patent was granted. Furthermore, the holder of a patent was required to manufacture in Canada within two years of the patent date, unless the patentee voluntarily agreed to grant licenses to Canadian manufacturers.

Under the new law, a patent is not automatically invalidated by reason of importation, and the working requirements, which are patterned after the British, are more liberal.

## WORKING REQUIREMENTS

A patent is now granted under certain conditions which may be summarized as follows, ignoring many of the finer points:

(a) The patentee shall manufacture the invention, or work the process, in Canada sufficiently to satisfy the reasonable requirements of the public.

This implies that one need not work the patent until there is a public demand for the invention. Hence an inventor of a new product is no longer under any compulsion to manufacture in Canada within a specific time limit whether or not his manufacturing and marketing plans have been developed.

(b) Any interested person may petition the Patent Commissioner, stating that the reasonable requirements of the public have not been satisfied, and ask that the patentee be ordered to supply the patented article at a reasonable price or to grant licenses for using the invention on reasonable terms.

(c) If the parties do not come to an agreement, the Commissioner may, after giving a hearing, order the patentee to supply the article within reasonable limits at a price fixed by the Commissioner or to grant a license. This must be done within a specified time limit on pain of forfeiture of the patent.

(d) Such an order shall not be made within three years of the patent date, or before June 13, 1924; nor will it be made if the patentee gives satisfactory reasons for his default.

(e) The reasonable requirements of the public shall not be deemed to have been satisfied:

If any trade or industry in Canada is unfairly prejudiced by the patentee's failure to supply the article or carry on the process; or

If the patentee will not grant a license on reasonable terms; or  
If he attaches unfair conditions to the purchase or use of the invention.

(f) Not less than three years from the date of the patent grant, and after June 13, 1924, any one may petition the Commissioner to have the patent revoked on the ground that the invention is being worked mainly outside of Canada.

(g) In such a case, if the patentee cannot furnish a satisfactory excuse for not manufacturing in Canada, the patent may be revoked at once, or after a reasonable interval, unless the patentee has begun working operations in Canada by that time.

These provisions of the patent law are new and have not been clearly interpreted as yet, but it is to be noted that the Commissioner has been given wide latitude and discretion in the matter. Since patentees living in this country have not been unduly oppressed in the past, and since the new law is less drastic than the old, it is fair to assume that the Commissioner will apply the law reasonably and without imposing a heavy burden on United States inventors and manufacturers.

## PATENT APPLICATIONS

Since Canadian patent practice differs considerably from that on this side of the line, a resumé of some of its main features as now required seems worth while. Ordinarily, an American files his patent application first in this country; hence the law affecting such cases should be particularly noted. The main requirements are that:

(a) The patent application in Canada must be filed within one year after the filing date of the United States application.

(b) The invention must not have been patented or described in any printed publication more than two years before the date of filing in Canada.

(c) The invention must not have been in public use or on sale in Canada for more than two years before the filing date.

It should be noted that public use or sale in any country other than Canada does not affect one's right to a patent, whereas a published disclosure of the invention in any country counts against him. The inventor may use or sell his invention in the United States for more than two years before filing in Canada, but he must be careful that no description of the invention has been published anywhere in the world for that length of time, if he wishes to obtain a valid patent.

In order that the new law may not work undue hardships on applicants, it gives until June 13, 1924, within which time inventors who have already filed United States applications may file their Canadian cases, providing the requirements concerning two years' public use, sale, and printed disclosure are satisfied. The law in regard to filing such applications where a United States application has been filed for more than a year may be summarized as follows:

(a) If no United States patent has been granted, the Canadian application must be filed before June 13, 1924.

(b) If a United States patent has been granted the Canadian application must be filed within one year from the date of the patent and before June 13, 1924.

The Examiner does not search any but Canadian patents; hence it is always advisable to file the United States application first and get the benefit of the search made at Washington before the Canadian case is filed. In fact, it is wise to hold up the latter after filing until the patentability of the claims in this country can be determined, so that the Canadian claims may be made to correspond with those in the United States case.

Since the Canadian Office does not print its patents, the applicant is required to file duplicate copies of the specification and drawings, as well as a third copy of the drawings and of the patent claims. One of the duplicate copies of the complete application is held in the Patent Office when the patent is granted, and the other copy is attached to the patent-granting paper and returned to the inventor. When one wishes to obtain copy of such patent, it is necessary for the Patent Office to make a typewritten or photographic copy of the specification and a photograph of the drawings for such purpose. This costs \$4.00 as against ten cents for a United States patent.

## FOODS AND MEDICINES

Of direct interest to chemists, it may be noted that if the invention relates to a food or medicine prepared by a chemical process, the inventor should claim the method of manufacture and he may not claim the substance itself, except when produced by the special method described and claimed.

<sup>1</sup> Received October 6, 1923.

Each patent for the preparation of a food or medicine shall be subject to a compulsory license granted by the Commissioner. Any person applying for this license may be permitted to use the invention for the production of food or medicine, but not otherwise. So wide are the powers of the Commissioner that he may settle the terms of the license, the law merely stipulating that he have due regard to the desirability of placing the substance in the hands of the public and at the same time giving the inventor a proper reward for his invention.

#### INTERFERENCES

If two independent inventors file applications covering the same invention, a board of arbitrators shall be appointed to award the patent to one of the claimants. In the United States, such a decision is rendered by a special official in the Patent Office, from whose decision one may appeal to various other officials and the courts. In Canada, one of the arbitrators is chosen by each applicant and the third by the Commissioner. If either applicant fails to choose his arbitrator, the patent shall issue to the other. If there are more than two claimants, the Commissioner may appoint the three arbitrators, provided the claimants do not unite in selecting them. The arbitrators are given the full powers vested in a Civil Court to investigate the matter and the award signed by any two of the three arbitrators shall be final.

#### RESTORATION AND REISSUE OF PATENTS

If a Canadian patent has become void under the terms of the old patent act, through failure to pay fees or to manufacture in Canada or because of importation, the patentee has a chance under the new act to have his patent revived within two years from the date of its becoming void, but any third party who has commenced lawfully to make, use, or sell in Canada, during

the period when the patent was void, may continue to use the invention just the same as if the patent had not been revived.

A reissue to correct inadvertent mistakes in a patent must be obtained within four years from the date of the patent; but any patent which is now alive may be reissued if the application is filed before June 13, 1924. This provision is important, since it gives a patentee whose Canadian patent was granted before his United States patent an opportunity to revise the Canadian patent in agreement with the other case and thus incorporate in it such claims as have stood the test of patent searches in this country.

#### VALUE OF A CANADIAN PATENT

Canada is a country of about 9,000,000 people and has over 40,000 miles of railroads. In many industries its importance for manufacturing purposes is far out of proportion to its population, since the United Kingdom is its market. The decision, therefore, whether or not to take out a Canadian patent should be made only after considerable study into the advantages of manufacturing in Canada, or of licensing a Canadian under the patent, as well as the particular conditions which affect the market in Canada and the British Empire.

Since the patent cannot be attacked for at least three years, that period may be sufficient for one to get his market established. If an application is filed the patentee thereby secures a period of grace within which he may decide as to the value of Canadian patent protection. He can then take his time in analyzing the problem as to whether he will manufacture in Canada, grant licenses or merely do nothing and wait until the patent is attacked before taking any steps to work the patent. The last course is one that is often adopted with reference to British patents. Undoubtedly, a Canadian patent is worth while in a large number of cases.

## Personals

Alan R. Albright has resigned his position in the Jackson Laboratory of the E. I. du Pont de Nemours & Company to organize a research laboratory for Gumpert & Co., Brooklyn, N. Y.

Raymond F. Bacon, C. H. Kidwell, and Elizabeth N. Kidwell have reorganized the firm of Kidwell & Bascom, Inc., under the name of Kidwell & Co., Inc., chemists and chemical engineers. The newly elected officers of the company are: C. H. Kidwell, president and treasurer; Raymond F. Bacon, vice president; Elizabeth N. Kidwell, secretary. The company will continue its research and consulting business at its office and laboratory at 27 Thames St., New York City.

Andrew Balfour, for the past ten years director-in-chief of the Wellcome Bureau of Scientific Research, London, resigned on October 31. C. M. Wenyon, who for the past nine years has been director of research in the tropics at the Wellcome Bureau of Scientific Research, has been designated as his successor.

Joseph S. Bates, formerly manager of the Research Division of the Marcus Hook, Pa., plant of the National Aniline & Chemical Co., is now employed by the Textile Service Co., Philadelphia, Pa.

Russell W. Brandt, formerly development chemist for the U. S. Gypsum Co., Fort Dodge, Ia., has taken charge of the chemical work of the General Fireproofing Co., Youngstown, Ohio.

Samuel Byall, formerly assistant research chemist at the sugar mill of Penick & Ford, Marrero, La., has resigned to become chief chemist of the International Sugar Feed Co., Memphis, Tenn.

P. G. Daschavsky, senior and supervising chemist of the laboratories of the Cudahy Co., Omaha, Neb., has found it necessary to take an indefinite leave of absence on account of continued ill health.

F. S. Dickson has resigned his position as assistant to the president of the Synthetic Organic Chemical Manufacturers Association, New York City, to go into private business.

Richard Fischer, formerly of the Chemistry Department of the University of Illinois, has accepted a position as research chemist at the laboratories of the Combustion Utilities Corp., Long Island City, N. Y.

H. C. Howard has been appointed assistant professor of chemistry in the Department of Chemistry, University of Missouri. For some time Dr. Howard has been research chemist on the staff of the B. F. Goodrich Company.

Karl G. Krech has recently been appointed assistant process superintendent of the new Parco refinery of the Producers & Refiners Corp., Parco, Wyo.

Max Kuniansky, formerly analyst for the American Cast Iron Pipe Co., Birmingham, Ala., has accepted a position as chemist with the Lynchburg Foundry Co., Lynchburg, Va.

The honorary degree of doctor of science was conferred by the University of Liverpool upon G. N. Lewis, professor of chemistry, University of California, during the recent meeting of the British Association for the Advancement of Science.

James W. Martin has recently resigned from the employ of the Union Carbide & Carbon Chemical Corporation to accept an appointment as assistant to the general superintendent of the Jones & Laughlin Steel Corp., Woodlawn, Pa.

August Merz, of Heller & Merz, has been elected chairman of the dyestuffs section of the Synthetic Organic Chemical Manufacturers Association, New York City, to fill the vacancy caused by the death of Fred E. Signer.

William B. Plummer, formerly research chemist for the Grasselli Chemical Co., is now associated in the same capacity with the Combustion Utilities Corp., Long Island City, N. Y.

L. W. Ryan, who for the past nine years has had charge of the research laboratory of the Lindsay Light Co., Chicago, is now employed as research chemist for the Titanium Pigment Co., Niagara Falls, N. Y.

Otto M. Smith has accepted the position of professor of chemistry at the Oklahoma Agricultural and Mechanical College, Stillwater, Okla. During the past year he was connected with the chemical department of the Iowa State College.

Richard Sneddon has left the employ of the Dominion Flour Mills, Ltd., Montreal, where he has been employed as chief chemist for the past two years, to go to California for his health. John Miller, formerly chemist for the Shelly Bakeries, Vancouver, B. C., has been designated as his successor.

# AMERICAN CONTEMPORARIES

## John Uri Lloyd

TO KNOW a man you must see him at his work. To do this in the case of John Uri Lloyd you amble down a quiet side street in Cincinnati and find the pharmaceutical manufacturing concern of Lloyd Brothers—three of them, one of whom seems to watch over the more impractical two, a second who is constantly at molds and never at business, and the third who is the subject of this sketch. To find him, you enter the business office where fast work is necessary if advance is to be made. Better an appointment ahead or else some twenty voices are likely to carry the information that the "Professor," as he is rightly, appreciatively, and affectionately called, is off the premises with no prospect in the visitor's life of return. And when a man's soul is in the spirit world is this not the truth? But if you can give the right sign—and an ability to discuss mass action is a better one than salesmanship—a friendly hand from a brother, a secretary, or a production manager urges you through a door. You choose between walking up four flights or taking the freight elevator. Again you feel lost until "Edee," who is at once cheerful presence, technical assistant, and guardian lion to the Professor, guides you with gentle voice through dark corridors into one of two or three cubicles, immaculately clean, spotlessly in order, and strictly at work. And here, either from his desk or from over some beakers the Doctor of Science, *honoris causa*, or the "Empiricist and Irregular," as he calls himself, welcomes you.

I do not remember a time when, either alone or with a group of scientific friends, there was not in his first words a note of appreciation for *their* endeavors—a proof at once of his first-hand knowledge of the other man's life and the catholicity of his thought, for politicians, practical men, and theorists who put the modern builders of the atom to shame, all seek him out. Such greeting is followed by, "May I tell you a story?" And then some pearl, fitting well into the setting of the moment, is brought forth from his seventy-odd years of oyster life which even the great must pass through. In the pause which follows he speaks again: "I have prepared an experiment which I should like to show you." In those who have had this experience several times, a warm rush of blood to the head is the emotional response which foretells that now some new decoration will be knocked off their scientific gargyle. Do you hold the Guldberg-Waage law all sufficient; is the "dew" on plants a settled question for you; do you think that the tincture preparer of 1850 knew everything; is your view of solubility a crooked one because you know only water; is water itself just  $H_2O$  to you; is biology and undertaking confused in your mind; are you sure that you know where the alkaloids come from; do you know why plants are green, or sometimes red, or maybe black; or why flowers are white and sometimes yellow? Answer carefully if your philosophy, your faith, or your religion are built up on the demonstrable in nature and not upon the interpolated texts of our scientific cook-book makers.

As you wait for a solution to filter, your eyes wander into the background. What are those vials labeled *a* to *d*? "Just

alkaloids separated from ———." And what are those labeled I to IX. "Another set from ———." But you were sure that each of these infernal plants contained but one alkaloid. Quite so, but here are the rest. And knowing that fat reputations have been built upon the discovery of just one alkaloid,

you ask when the Professor will publish his results. "I am not young any more and a bit tired. Let me tell you about them and then you publish the facts." You see on the table a pot of tar-like material. And what is that? "Just the muck which you 'regulars' think it well to carry along with the bits of active material in your standard pharmaceuticals and which, after twenty years of work, I have learned to get out by my studies of differential solubility." You feel that you have heard just an overtone of bitterness in his voice, but a look at his face seems to belie your impression.

You digress from the material of the demonstration to its philosophic consequences, and philosophic consequences join quite naturally to the business of life itself. Is science a cloak to you which may be put on and off during convenient working hours? If so, John Uri Lloyd does not interest you for to him it is life itself. Do you find her a yoke gladly to be cast aside were the rewards of labor not so necessary? Again our man

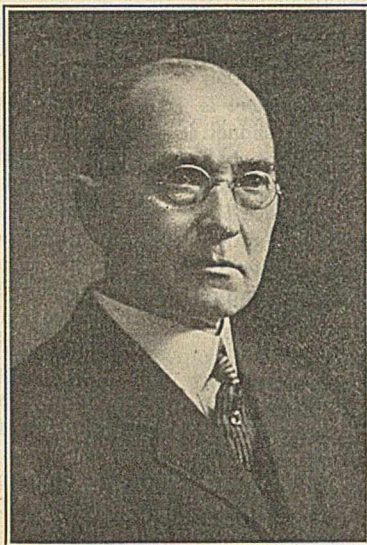
does not interest you for he follows her as lovers, romance; and children, the rainbow. Alkaloids are not things to be made into medicine, but voices which speak from another world. To be a practical man of chemistry is simply to ease the material life of a fellow that he may enjoy better the fruits of the spirit.

You rise to go. You find your way out as you came in, but you are not as conscious as you were of the externals. You are more conscious of the internals. You have lost something—some of your scientific prejudices, some of your party adherences, some of your reverences for mere tradition. Also you have gained something—a more mobile state of mind, a larger tolerance, an increased generosity. And you are conscious that this is because for a little while you have been away from commissions, committees and boards, from diagrams, formulas, and fudge, and from canned efficiency, officialism, and Main Street, and for the same length of time have lived in the presence of the one thing that moves our universe, an individual and a man who is as good a picture in flesh and blood of what science stands for as may be found in the day's journey.

MARTIN H. FISCHER

## New Tabular Data

The Editorial Office of International Critical Tables has just finished the preparation of a table of the viscosity of water at 1-degree intervals between 0° and 100° C. This table is based upon a very thorough and critical evaluation of all the data available on the subject. While prepared primarily for the use of Cooperating Experts of International Critical Tables, a number of extra copies are available for distribution at 5 cents (stamps) each. Copies of the 16-page pamphlet, entitled "Fundamental Constants and Conversion Factors," are also available at 25 cents (stamps) each. This pamphlet contains the latest data on the fundamental constants of nature, including definitions, dimensional equations, conversion factors, etc.



JOHN URI LLOYD

## SCIENTIFIC SOCIETIES

### Meeting of American Electrochemical Society

TWO features mark the forty-fourth meeting of the American Electrochemical Society, at Dayton, Ohio, September 27, 28, and 29, 1923, as probably the most important meeting which this Society has held. Round-table discussions of four of the major problems of the electrochemist, held behind virtually closed doors, at which all interested were invited to discuss freely and openly their problems and results, brought out an immense store of information and opinion with direct practical bearing which could not have been gotten in formal papers. The symposium on gaseous conduction, which occupied the entire second day of the meeting, brought together in one place practically all the present-day knowledge of this subject from both physicists and physical chemists.

The first session of the Society, held at the Hotel Miami, was devoted to the address of welcome by Charles H. Paul, president of the Engineers' Club of Dayton, and to the reading and discussion of six papers. Water-line corrosion was the subject of a paper by Kenneth M. Watson, which was discussed with much interest from the floor. M. A. Hunter and A. Jones have studied the reduction by sodium of various rare metal chlorides, particularly those of beryllium, chromium, zirconium, uranium, and vanadium, and suggested that this method offers a possible commercial process for producing these metals. George S. Tilley and Oliver C. Ralston followed with a discussion of electrometric methods of following hydrolytic reactions. Three papers from the research laboratory of the Westinghouse Electric & Manufacturing Company dealt with various phases of insulating and impregnating compounds used as insulators and the effect of age and heating on these. E. J. Casselman discussed the phenol-formaldehyde group; H. C. P. Weber, the varnish group; and D. E. Howes, various impregnating compounds.

Luncheon the first day was served to four groups at the Engineers' Club and was followed by round-table discussions. H. W. Gillett, of the Bureau of Mines, presided over the most interesting discussion of the group considering "Electric Furnace Brass Foundry Practice." This group consisted of representatives of the central power companies, and the designers, builders, and users of electric brass furnaces. Walter Fraire presided over the symposium on the "Development and Future of Electrodeposition;" T. J. Thatcher, over that on "Organic Electrochemistry;" and A. H. Hooker, over that on the "Utilization of Chlorine." These round-table discussions were so successful that they will be made a regular feature of the Society's meetings.

Those not detained by the round-table discussions were the guests of the local committee on a tour of inspection of McCook Field, the engineering station of the U. S. Army Air Service, and of the Miami Conservancy, the immense project which has been completed with the idea of preventing the recurrence of the floods which formerly caused much damage to the district around Dayton.

Thursday evening was devoted to a picnic dinner and smoker at Triangle Park. The feature of this dinner was the informal address of Chas. F. Kettering, president of the General Motors Research Corporation, on the future of research. In a most picturesque way, Mr. Kettering appealed for closer cooperation between the workers in the various fields of science. "What we need," he said, "is correlation among the so-called sciences.

All of us are studying merely the relations of mass and energy." His plea was for the reduction of the expression of results to commonly understandable terms, rather than "the foreign languages" in which chemists, physicists, engineers, astronomers, and so forth, now express the same simple relations. He was quite vehement in his protest against "recognized authority," which he said did not exist, and stated that the more standardized an industry is the more fertile a field it offers for research.

Friday's sessions were devoted to a symposium of sixteen papers on the various aspects of gaseous conduction, under the chairmanship of Duncan MacRae. Its importance can hardly be overestimated, particularly when it is considered that papers from Holland, England, Canada, and Germany were included. The application of these studies to the X-ray, radio, and the electric lighting and electric arc industries was brought out. H. B. Wahlin brought the symposium to a fitting close with an experimental address on recent work in this field.

An intensely interesting program on the electrodeposition of metals occupied the session of Saturday morning. Papers from the Bureau of Standards, University of Pennsylvania, Niagara Electrochemical Company, Massachusetts Institute of Technology, Columbia University, University of Wisconsin, and the Northampton Polytechnic Institute of London, formed part of this program.

The spring meeting of the Society will be held at the Bellevue-Stratford, Philadelphia, Pa., April 24, 25, and 26, 1924. The subjects to be discussed will include electric furnaces, recent progress in electrodeposition, and organic electrochemistry. Round-table discussions will be held as at the Dayton meeting.

### Societies Elect Officers

At the annual meeting of the Technical Photographic and Microscopical Society, held at Grand Central Palace, New York City, September 21, 1923, the following officers were elected:

*President:* EMILE M. CHAMOT  
*Vice Presidents:* FRANK V. CHAMBERS, HENRY GREEN, and ARTHUR W. CARPENTER  
*Secretary-Treasurer:* ALFRED B. HITCHINS  
*Executive Committee:* Officers, and F. F. RENWICK and LLOYD I. SNODGRASS

George K. Burgess, director of the Bureau of Standards, was elected president of the American Society of Steel Treating at the association's annual convention. The other officers named were: vice president, R. M. Bird; treasurer, Zay Jeffries; and director, J. F. Harper.

### Calendar of Meetings

American Mining Congress—New York City, November 5 to 10, 1923.  
 Association of Official Agricultural Chemists—39th Annual Convention, Washington, D. C., November 19 to 21, 1923.  
 American Institute of Chemical Engineers—Winter Meeting, Washington, D. C., December 5 to 8, 1923.  
 American Electrochemical Society—Spring Meeting, Philadelphia, Pa., April 24 to 26, 1924.  
 American Chemical Society—67th Meeting, Washington, D. C., April 21 to 25, 1924.

## NOTES AND CORRESPONDENCE

### Sell Chemistry to America

Many chemists and physicists bewail the fact that their contributions to progress are neither understood nor appreciated and that their status in the mind of the general public is a lowly one.

At the third annual dinner of the Salesmen's Association of the American Chemical Industry, Charles H. Herty, president of Synthetic Organic Chemical Manufacturers Association, remarked that his hearers carried the chemical industry in their grips and urged them to sell it to America. Every salesman knows that it is easier to sell an article that has been well advertised than one that has had little or no publicity. At the same function Edgar Fahs Smith, provost emeritus of the University of Pennsylvania, the guest of the evening, urged the recognition of chemistry's claim as "the most human science," one that served each and every one in countless ways every day.

For the lack of recognition accorded chemical industry the chemist himself is largely to blame because he has failed to advertise the service he renders. When you meet a man who says he is a civil engineer, at once you visualize the one who builds roads through forests, spans rivers, and tunnels mountains. Parallel concepts arise when you meet the mechanical, electrical, or mining engineer. Those in other professions—doctors, lawyers, architects—all occupy positions of esteem in the mind of the public they serve, because every day that public sees examples of their products and knows them for what they are. But when Mr. Average Citizen meets one who styles himself chemist he pictures a pill-roller, or, ascending the scale of his imagination, one who can tell him how to detect wood alcohol in the bootleg he buys.

The chemist and physicist bewail the fact that they are not accorded the respect that is justly merited through their services to American industry, and yet make no well-directed or concerted effort to establish the status they claim in the public mind. Every one knows that Gustav Lindenthal conceived Hell Gate Bridge, Cass Gilbert the Woolworth Building, and A. J. Cassatt the Pennsylvania Tubes and Terminal, but how many know a single name of the many chemists and physicists, who, by long painstaking research, produced steel and cement of a quality that made possible those monumental achievements. The public accepts as a matter of course that its supplies of milk and water shall be pure and wholesome, that its foods shall be unadulterated and nourishing—what chemist has ever tried to advertise the service his science renders here? Metropolitan life as it exists today could not have been evolved had it not been for the services rendered by our chemists and physicists which alone have made possible the type of buildings in which we live and work, the kind of clothes we wear, and even modern systems of transportation and communication—and yet, relatively few people realize these facts. The day should not be very far distant when every industrial exposition held in this country should have an AMERICAN CHEMICAL SOCIETY booth, wherein will be shown, in a manner calculated to win popular attention, the principal contributions of chemistry and physics to the science, art or business whose interests are being served by that particular exhibition.

Although chemistry and physics are fundamental sciences and are employed in every industry, their importance is not grasped because their influence on ultimate products is obscure. This is particularly true if the final product happens to be one of an art or science which because of its very limitations can be

clearly defined. In order to demonstrate the full measure of service that chemistry renders, one would have to show a cross section of all industry, a task manifestly impossible. On the other hand, it would seem practicable, if the physicists, chemists, and chemical engineers are really desirous of establishing themselves on a higher plane in public esteem, to assemble an exhibition or exposition of great popular appeal which would have a high educational value and, in addition, be an inspiration to all scientists. Especially would such an exposition be practicable were cooperation assured by all those engaged in industries that owe their existence to physicists and chemists.

There is hardly a single phase of American industrial or commercial activity which does not have its association. The Department of Commerce in "Commercial and Industrial Organizations of the United States" arranges the national and international organizations listed under one or another of seventy-one classifications. To research and development in chemistry and physics at least one-half of the industries so classified owe, if not their very existence, a large measure of the knowledge that makes them preëminent. There are no less than one hundred and nine societies or associations in the United States representing industries that are the product of the science of chemistry alone. Through the influence of chemists who are members of these organizations it should be possible to bring them all together for united effort in assembling an exposition such as is suggested. Among these organizations there are widely divergent interests and aims, but fundamentally all are the children of the science of chemistry. Probably the most logical body to take such a project in charge and to bring together all the different interests would be the Section of Chemical Education of the AMERICAN CHEMICAL SOCIETY.

There has been some criticism of the Ninth National Exposition of Chemical Industries, because it had little popular appeal and so enhanced the importance of the chemist but little in popular estimation. The critics lose sight of the fact that the exposition was made possible in large part by those desirous of establishing contact with prospective customers and that this purpose was served to the satisfaction of those most interested.

Consider the facts, because with facts before one, most problems answer themselves. If, as some critics contend, the chemist and the physicist are rated unfairly in popular esteem, is it because a perverse public refuses credit where credit is due, or, as seems more probable, because the exponents and practitioners of the twin sciences have encased themselves in cocoons of hieroglyph instead of spreading clear webs of expression to catch the popular imagination? When once the facts are understood and a sincere desire is awakened in each and every one concerned to correct the condition, then many opportunities will be found to establish the physicist and chemist on the plane to which they are entitled.

PAUL MC MICHAEL

NEW YORK CITY  
October 15, 1923

### The Fourth International Congress of Chemistry—Correction

In the article under this title [THIS JOURNAL, 15, 1083 (1923)] under Section VIII, the conversion factor should read: 1 calorie 15° C. = 4.184 joules.



## Determination of Ash, Arsenic, Copper, and Zinc in Gelatin

*Editor of Industrial and Engineering Chemistry:*

We have read with much interest, the article of Roger M. Mehurin, entitled "Determination of Ash, Arsenic, Copper, and Zinc in Gelatin" [THIS JOURNAL, 15, 942 (1923)]. As a result of the analyses in our laboratories of some ten thousand samples of gelatin during the past fifteen years, we do not feel that the conclusions of the author of the above-mentioned article are warranted.

In the first instance, the amount of sample to be taken for analysis as recommended by Mr. Mehurin—namely, 10 grams—is entirely inadequate for the accurate determination of the minute amounts of copper and zinc present in most samples of gelatin; and in many cases this also applies to the determination of arsenic. It follows, then, that on a suitably large sample, 50 to 100 grams, the ashing procedure is impractical. We have found from our experience that the methods as outlined by the Association of Official Agricultural Chemists, in *J. Assoc. Official Agr. Chem.*, 5, 343 (1922), and revised to date by Claude R. Smith, of the Bureau of Chemistry, offer a simple, reliable, and accurate method of procedure for the determination of the above-mentioned impurities.

We have found that, if ordinary care in manipulation and proper technic are used, there is never any difficulty experienced in the saturation of the solution with hydrogen sulfide, nor in its subsequent filtration.

Referring to the statement in the article by Mr. Mehurin, that "the determination of copper by titration with sodium thiosulfate is open to a considerable error because of the difficulty in obtaining a definite end point when small amounts of copper are titrated," we do not agree with the author in this respect. This objection has often been raised in our experience, and we have always been able to demonstrate that with proper technic it is possible to obtain end points which are sharp and remain so for half an hour or more. Furthermore, numerous blank and check determinations have shown conclusively that the method can be relied upon to give accurate results.

We have no criticism to make of the method for the determination of arsenic given by Mr. Mehurin, as we do not feel that there is any very essential difference between it and the A. O. A. C. method.

IRVING HOCHSTADTER

HOCHSTADTER LABORATORIES  
NEW YORK CITY  
September 12, 1923

*Editor of Industrial and Engineering Chemistry:*

Referring to Mr. Hochstadter's letter of September 12, published above, it will be noted that a 20 to 40-gram sample of gelatin, and not 10 grams, is specified for the determination of copper and zinc. In the tentative A. O. A. C. method referred to by Mr. Hochstadter, and of which he approves, practically the same range of sample is used—namely, 20 to 50 grams—and in the Hertwig method [*J. Assoc. Official Agr. Chem.*, 7, 41 (1923)] a 20-gram sample is specified. No such range of sample as 50 to 100 grams is mentioned in any method for the analysis of gelatin and glue that has come to the attention of the writer. Since the metals are usually in solution with the gelatin during manufacture, they are uniformly distributed in the finished product and therefore as little as 20 grams of the mixed sample will usually be found sufficient.

A perfect ash will be obtained if the directions are followed, and as many as twenty samples can be added directly to a furnace 4 x 6½ x 16 inches without previous charring and without

requiring any attention whatever during the ashing process. From this point it has been the experience of the writer that an appreciable time is saved in handling small volumes of solution containing small amounts of inorganic salts rather than large volumes containing large amounts of organic material.

In regard to the copper determination, the writer has often experienced difficulty, as have others, in obtaining a definite end point when titrating very small amounts of copper with thio-sulfate, and has obtained much more uniform results with the colorimetric method.

In conclusion, it may be stated that the method was not offered with any intention of supplanting or criticizing the accuracy of the tentative A. O. A. C. method (with the possible exception of the above-mentioned copper titration), but merely with the thought that it would be found to be less time-consuming in cases where it is necessary to analyze a large number of samples simultaneously. In this connection it may be mentioned that this method has been employed for some time past, in preference to all others, by the laboratory of one of the largest gelatin and glue works in the country.

R. M. MEHURIN

BUREAU OF ANIMAL INDUSTRY  
WASHINGTON, D. C.  
September 17, 1923

## New Treatment for Gasoline

In his address before the Mid-West Section of the Society of Automotive Engineers in Chicago, October 12, C. F. Kettering, president of the General Motors Chemical Company, announced that this company and the Standard Oil Company (Indiana) had entered into a contract for the distribution of ethyl fluid.

Ethyl fluid is the new addition agent for gasoline, and has the effect of increasing engine efficiency and taking the knock out of an engine, no matter under what conditions or load an automobile is driven. It is the result of several years' research and test at the laboratories of the General Motors Research Corporation in Dayton, and has met with enthusiastic reception from motorists in Dayton and in Cincinnati, Ohio, where it has been placed on sale at a few stations.

Gasoline treated with ethyl fluid has a characteristic light wine color, which distinguishes it from other automobile fuels.

Distribution by the Standard Oil Company (Indiana) will cover the States of Indiana, Michigan, Illinois, Minnesota, Wisconsin, Iowa, Missouri, Kansas, South Dakota, and North Dakota as soon as installation can be made. The southern part of the distributing territory is being equipped this winter and the northern part will be equipped as early as possible in the spring, in order that motorists may be supplied when the 1924 motoring season opens. It is believed that all the Indiana company service stations will be open and ready to supply the treated fuel by July 1, 1924.

## Dictionary of Specifications

The work which the Bureau of Standards is carrying out on a dictionary of specifications has made good progress. During the past month existing specifications have been collected from more than 75 per cent of the important national technical societies, trade associations, and governmental publishing agencies that have issued specifications. Leaving out all duplications, it would appear that about 5000 specifications are available from these sources. However, not all of these specifications can properly be classed as related to commodities purchased by the Federal, State, and Municipal Governments and public institutions. It is believed that about 20,000 commodities do come within this class and of these more than 75 per cent of all commodities purchased for Government consumption are not covered by available specifications.

Work is being expedited on the collection of existing specifications with the object of making the collection as complete as possible so that the first step in the preparation of the dictionary, the issuance of a classified list of existing specifications, may soon be taken. This will be of considerable service to all agencies interested in this subject, and with the coöperation of the advisory board will be used as the basis for selection of specifications for inclusion in the dictionary.

# WASHINGTON NOTES

## KEEN INTEREST IN CHEMISTRY

If the first meeting of the Local Section, which was held at the Cosmos Club on the evening of October 11, can be taken as a criterion of what is to follow, the coming winter may easily become a record one so far as things chemical are concerned. Over one hundred and sixty chemists were present, thus making the meeting one of the best attended in the history of the section. E. W. Washburn was the speaker of the evening, lecturing on "Physical Chemistry and Ceramics." After his address the meeting was turned into an informal reception to the following prominent chemists who have recently cast their lot with us: C. A. Browne, newly appointed Chief of the Bureau of Chemistry; George L. Coyle, who has come to Washington to head the Chemical Department at Georgetown University; S. C. Lind, chief chemist of the Bureau of Mines; J. E. Zanetti, chief of the Division of Chemistry and Chemical Technology of the National Research Council; and C. S. Hudson, who has returned to Washington after an absence of several years and is now connected with the Bureau of Standards.

As a further evidence of the steadily growing interest in chemistry, may be mentioned the following addresses before the Women's City Club on the evening of October 10: "The Romance of Chemistry," by H. E. Howe; "The Chemistry of Food," by W. W. Skinner; and "Chemistry in Business," by F. B. Gorin. Again, on the evening of October 17, L. I. Shaw, of the Bureau of Mines, addressed the Piney Branch Citizens Association, choosing "Helium" as his subject.

## ALCOHOL TRADES ADVISORY COMMITTEE ISSUES REPORT

The proposal to create a separate bureau of government for the enforcement of prohibition, independent of departmental control and answerable only to the President, is condemned in a report submitted to the Bureau of Internal Revenue by its Alcohol Trades Advisory Committee, composed of eleven representatives of scientific societies and industries in which alcohol is an indispensable chemical raw material. The committee claims that such a procedure would be contrary to long-established practice under our system of government and that it would seriously handicap scientific research and lawful industry. The committee showed that a similar scheme was incorporated in the Ernst-Wood Bill (H. R. 12035-S. 3713), introduced in the last Congress, which was opposed by all scientific bodies and legitimate trades and failed to be even reported by the House Judiciary Committee after an open hearing. They add that "the proponents of such a bureaucracy may be assured that it will be opposed with every ounce of energy that can be put forward by those engaged in lawful professions and businesses in which the chemical alcohol is required and used."

The report points out that in the World War the production of nonbeverage alcohol was rated as one of the nation's "key industries" and "is admittedly a basic chemical essential to our national defense, industrial and economic development, and even to the advancement of civilization itself." A comprehensive chart and other data showing the innumerable scientific and industrial uses of alcohol are appended to the report. It asks "from where is the essential future supply of alcohol for governmental, industrial, and scientific purposes to come? Under present conditions of prohibition law enforcement we have real cause to be concerned."

The committee characterizes the attacks upon the Secretary of the Treasury and the Commissioner of Internal Revenue as being as unfair as unwarranted, both of those officials having but properly and justly exercised their statutory right of review. It states that the action of the Government in placing in the hands of a Prohibition Commissioner without essential technical and economic training the duties of carrying out the Congressional mandate to promote the use of alcohol in scientific research and development of lawful industries, was illegal by implication, illogical by any method of sound reasoning, economically impracticable, and should be forthwith corrected. The committee recommends that the Commissioner of Internal Revenue designate a deputy commissioner or appoint an industrial alcohol commissioner to take over the administration of that phase of the law. In this way, they claim, efficient and scientific administration would be assured and at the same time the Prohibition Commissioner would be relieved from routine work incidental to serving legitimate industry and could devote the

necessary time to his logical police duties. The committee states, "we yield to no one in our adherence to the principle of law enforcement, but surely the National Prohibition Act can be so administered as not to interfere with the health, economic needs, and the national defense of the country."

## TARIFF COMMISSION HEARINGS

Final argument on the application of coated paper manufacturers for a 50 per cent reduction in the present duty of 2.5 cents per pound on casein was heard on September 25. Henry A. Wise appeared as counsel for the consumers of between 75 and 85 per cent of the casein used in this country, and argued for a lower tariff rate, declaring that casein was absolutely necessary to the coated paper industry since domestic production had never been adequate.

The hearing on rare sugars and amino acids, scheduled for September 27, was adjourned because no witnesses appeared.

On October 6 final arguments were presented for an increase of 50 per cent in the duty of 3 cents per pound on sodium nitrite. No facts relative to costs of production were presented, but the greater part of the time was consumed by an argument by former Senator McCumber, attorney for the American Nitrogen Products Company, and joint author with former Representative Fordney of the 1922 Tariff Act, on the procedure to be followed by the Tariff Commission. Mr. McCumber argued that the commission has no authority to recommend conclusions to the President, but must confine its duties to investigations and the submission of reports based on field work and hearings; that the President is not bound to accept the findings of the commission, but may call upon any other agency for additional reports or advice; and that witnesses at public hearings should not be cross-examined by any one except the commissioners.

Other hearings of interest to chemists and thus far announced by the commission are: Oxalic acid, November 5; diethylbarbituric acid and its derivatives, November 7; barium dioxide, November 9; logwood extract, November 12; potassium chlorate, November 14; and sugar, January 15, 1924. In connection with the last-named hearing, the commission has announced a new policy in that on or about December 1 it will make available to interested parties a statement of the data secured on costs of production in the pending sugar investigation, as well as a statement of basic points and problems, as, for instance, the rate of interest allowed by the commission, depreciation allowances, etc.

## FOREST SERVICE EXPANDS

Two new experiment stations have been established under the provisions of the appropriations for the Forest Service made at the last session of Congress. One of these, the Northeastern Experiment Station, will have headquarters at Amherst, Mass., and operate in conjunction with the Massachusetts Agricultural College. The other one, the Lake States Forest Experiment Station, will have its headquarters at St. Paul, Minn., under a cooperative arrangement with the Minnesota Agricultural College. The establishment of these stations is in conformity with the program of the Department of Agriculture whereby each important forest region will be supplied with a station to handle local forest problems. It is expected that the forest experiment stations will aid the progress of forestry as much as the agricultural experiment stations have aided the progress of agriculture. S. T. Dana, formerly Forest Commissioner of Maine, has been appointed director of the Northeastern Station, and Walter H. Meyer, assistant. Raphael Zon will be the director of the Lake States Station.

## NATIONAL RESEARCH COUNCIL ENDORSES PRIZE ESSAY CONTEST

The Interim Committee of the National Research Council at its meeting on October 17 adopted the following resolution upon recommendation from the Division of Chemistry and Chemical Technology:

WHEREAS, The encouragement of the study of chemistry among high school students is of great importance in stimulating scientific interest among the generation which will later supply research workers in science, therefore, be it

Resolved, That the National Research Council considers the purpose of the Prize Essay Contest established by the American Chemical Society under the grant made by Mr. and Mrs. Francis P. Garvan as worthy of encouragement and approval.

## ENFORCEMENT OF THE NAVAL STORES ACT

The Bureau of Chemistry has distributed to the trade press, producers, factors, dealers, and users of turpentine and rosin, a tentative draft of proposed regulations for the enforcement of the Naval Stores Act of March 3, 1923. Twenty such regulations have been drafted and they are submitted for consideration and to permit those who desire to offer suggestions for amendment. Suggestions for amendment or requests for further information should be addressed to the Acting Chief of the Bureau of Chemistry, Washington, D. C.

Should the suggestions for amendment warrant, a date will be set for a public hearing at which any interested party will have an opportunity to advance arguments for proposed changes. Should no material amendments be suggested, however, it is probable that the regulations will be issued in approximately their present form, if and when approved by the Secretary of Agriculture.

Meanwhile, the Bureau of Chemistry is carrying on naval stores demonstration work in the South. The purpose of this work is to offer to individual producers of rosin and turpentine,

through visits to stills by a practical operator of good judgment, information as to the most practicable and profitable methods for the production of naval stores, and to aid them in solving technical problems involved in the manufacture of these commodities. It is believed that this work will aid the producers in complying with the act.

## FORESTRY ADVISORY COMMITTEE

Twenty leaders in the American pulp and paper industry have been asked by Secretary of Agriculture Wallace to form an advisory committee to work with the Department of Agriculture in formulating and carrying out its forestry policies which relate to the supply and use of timber in making paper and kindred products. It is thought that the creation of an advisory committee of men intimately concerned with the pulp and paper industry will be beneficial in dealing in a searching way with the fundamental problems of the industry.

October 22, 1923

## PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

## EFFECT OF JAPANESE EARTHQUAKE

The earthquake which devastated Japan has affected the market of chemicals in France. In the days which followed the announcement of the catastrophe, camphor, menthol, and oil of peppermint doubled in price. The celluloid industries were afraid that they would not be able to supply themselves, and the synthetic camphor factories, which are rivals of those of natural camphor, considered equipping themselves to increase their production.

When more circumstantial evidence was obtained, it was perceived that speculation alone had caused the rise in price since the camphor plantations are in Formosa and the market center at Kobe, far enough away from the stricken region so that the production of camphor could not be injured.

## NATIONAL FUEL

The decree obliging importers of oil to buy a corresponding amount of alcohol to constitute the national fuel is being vigorously enforced. It has been decided that in the interests of the development of the consumption of the national fuel, absolute freedom as to the price of oil and alcohol would be given to the manufacturers and importers. Contrary to expectations the minimum selling price has not been regulated.

In connection with this question of national fuel, it has been necessary to study the means of preservation of the alcohol or the alcohol-oil mixture. Preservation in tanks of great volume necessitate the dehydration of the air in the tanks. In fact, in damp climates atmosphere saturated with water vapor soon increases the water in the alcohol-oil mixture. The variations of temperature of this more or less humid air change the proportion of concentration of the alcohol or the stability of the alcohol-oil mixture.

To solve this problem, M. Dumanois proposes the addition of a small auxiliary reservoir to the large storage reservoir. This reservoir contains a large number of baffles and is filled with alcohol at 95° C. All the manipulations of the liquid in the reservoir cause the air to enter or leave through this smaller reservoir. The alcohol which it contains absorbs the water vapor of the air when the air is exhausted. Under these conditions only the dehydrated air can enter the large reservoir.

## FERTILIZER

It is well known that more nitrogen is used in the nitric form than in the ammoniacal form, but a satisfactory explanation to this phenomenon has not been given. It is estimated at present that the ammoniacal salts cause in the plant an acid secretion which is harmful to its development. By avoiding this secondary action by some means, with ammoniacal compounds a product always identical, sometimes superior, to that obtained by the nitrates would be obtained. The use of calcium salts, especially the carbonate and the sulfate, with the ammoniacal salts would permit these results to be obtained.

Czechoslovakia is developing considerably its agricultural industries and is therefore consuming increasing quantities of fertilizer. MM. Jahn and Prikes have carefully examined the

Czechoslovakian soil, and have succeeded in finding new deposits of potash. These deposits are estimated at 70 million tons as a minimum. They are particularly interesting for this country where the cultivation of the beet is extensive.

Moreover, the Czechoslovakian industries have just opened up at Prague an Experimental Institute of the Sugar Industry. This institute is divided into five sections: (1) Chemical Section, (2) Beet Section, (3) Physico-chemical Section, (4) Section of Hygiene of the Beet, (5) Machines Section. The originality of this unique institute devoted to the study of the beet and to the manufacture of the sugar consists in the fact that it is organized to receive technicians or chemists of other countries who desire to go there to study the latest methods of work accomplished at the institute.

## SCIENTIFIC CONGRESSES

Two important Congresses have been held—one at Strassburg, and the other at Bologna.

The Congress at Strassburg was held with the Pasteur Exposition and had for its object the study of refrigeration from the point of view of production and utilization. Of particular note were the explanations that were given to the utilization of freezing in the preparation of vaccines and in medicine. It was pointed out that it could be used advantageously to replace X-rays or radium in the treatment of cancer and tumors. Here is a field of unexplored work.

There was also proposed a means of using low and constant temperatures in research laboratories. Without descending to temperatures as low as those of liquid air, it is certain that in the investigations of temperatures between 0° and -50° C., the chemical reactions and phenomena are not sufficiently known and merit further study.

At Bologna was held the Fish Congress, destined to extend the use of this food. From the chemical point of view different interesting questions were taken up, especially the relations between the saltiness of the ocean and the migrations of fish beds, and, finally, on the chemical properties of fish oils, notably from the point of view of their richness in vitamins. The value of certain oils, especially the oil of cod liver, is attributed to their richness in vitamins, and it seems to be quite certain that the ocean is a medium particularly rich in all sorts of vitamins.

Along the same line, Mme. Randoin has recently pointed out that the source most rich in vitamins is the oyster. It is the antiscorbutic vitamin which the oyster contains in the proper proportions that has never been found before in a single living organism. The oyster could be a source of vitamins, not only for consumption, but to facilitate the investigations on their isolation.

## DEATH OF M. VIOLLE

M. Violle, dean of the Section of Physics of l'Académie des Sciences, has recently died. M. Violle studied the problems of radiation of bodies at high temperature. To him we owe the establishment, in 1884, of an absolute standard of light given out by a unit of surface of melted platinum, a standard which is universally recognized under the name Violle.

October 5, 1923

# LONDON LETTER

By HUGH GRIFFITHS, 15 New Bridge Street, London, E. C. 4., England

## KEY INDUSTRIES ACT

The unsatisfactory nature of the operation of the Key Industries Act is clearly exemplified by the decisions made in two recent cases. It has been decided by the referee that formaldehyde cannot be considered as a fine chemical, and it has accordingly been removed from the list of materials subject to duty. On the other hand, Rochelle salt is held to be a fine chemical, and is to be retained in the list.

These decisions, when all the evidence is read, sound to be fairly reasonable, but those familiar with the chemical trade will have a very natural feeling that there is something conflicting in the position which has resulted. A movement is afoot to get the whole basis of this act altered.

## RESIGNATION OF A. G. GREEN

A mild sensation has been caused by the resignation of A. G. Green from his position as director of research to the British Dyestuffs Corporation. It will be recalled that not very long ago two of the technical directors resigned. From the statements which have been made it seems pretty clear that the business men in this organization do not see eye to eye with the technical staff on the subject of expenditure on research, and while, on the one side, it is urged that the organization cannot support a very expensive research department, it is equally urged on the other side that unless the research proceeds the company cannot maintain its position.

This difficulty is one which is very common in this country at the present time, and although perhaps research work is now receiving more support than ever before, there is a feeling that business depression is making firms niggardly, and the only research which receives anything but the most grudging support is of a purely hand-to-mouth character, and investigations of fundamental matters are being left more and more to academic institutions. It must, however, be admitted that at the present time, when most chemical works in this country are feeling the effects of depressed trade, the cost of research organizations may eat up a large proportion of the gross profit. The only solution would appear to be to take a leaf from our neighbors—namely, in subsidizing research from the pocket of the taxpayer.

## NEW PLANT EQUIPMENT

At the Ship Building and Engineering Exhibition, the new stream-line filter is being demonstrated. In its simplest form this filter consists of a pack of paper sheets held together between distributing heads. The pack is perforated by a large number of holes. About half of the passages so formed are connected at one end to the feed chest in the lead of the press, and the remainder to the filtrate outlet chamber.

The filtration takes place at the edges of the paper sheets. It is stated that the paper employed is waterproof, that the apparatus therefore does not depend upon the porosity of the paper, and that the only apertures for filtration to take place are formed by the spaces between the sheets due to roughness.

When the apparatus was first described by Hele Shaw, it was thought that perhaps there would be difficulties in discharging the solids, but a very simple device has been applied to these presses, the tubular collecting spaces being fitted with small plugs which can be operated by the feed pressure to the filter. In a horizontal press it is consequently possible to discharge the deposited solids by the manipulation of valves, which cause the plugs to travel under the fluid pressure in either direction, so expelling the solid. It is stated that in many cases a fairly dry solid material can be obtained which is extruded from the apparatus as a continuous rod.

The most interesting feature of this apparatus is that most extraordinary claims are made regarding its efficiency as an ultra-filter. A solution of an organic dyestuff such as erythrosin can be passed through the press when the filtrate emerges absolutely colorless. This extraordinary result is stated not to be due to adsorption, and it is claimed that the feeding of the erythrosin solution can be continued without getting a colored filtrate. It is also claimed that when brine is passed through the apparatus a considerable proportion of the water can be separated from the salt, and it is stated that in this case the effect is not merely one of adsorption, but the salt is actually filtered out from the water. On theoretical grounds one would have thought that this would be impossible, as a system of

apertures sufficiently fine selectively to separate molecules of different sizes would be expected to render liquid flow almost impossible. It is suggested, however, that possibly salt forms some sort of hydrate complex with water, which makes this separation possible. It is, however, very extraordinary that salt will pass through a dialyzer such as the well-known osmogene, if simple filtration will effect a separation.

Apart from this astounding result, the apparatus would appear to have attractive possibilities for fine filtration work, and the compactness of construction is an attractive feature. A comparatively small and insignificant looking press is stated to be capable of filtration at the rate of 250 gallons per hour on a simple water solution, and owing to the small diameter of the passages employed the depth of the deposited layer of material is small, and consequently the effect of the thickness of deposit is not quite so great as in an ordinary filter press.

Some installations of this type, of considerable size, are at present under construction, and the results of these larger installations will be waited for with the greatest interest. This filter is reminiscent of the Plauson filter, but is very much cheaper in first cost, and only resembles the Plauson filter in having a laminated filtering medium.

A new mill, known as the premier mill, has recently appeared, which is used for mixing, emulsifying, and very fine disintegration. In its application this machine resembles to some extent the colloid mill, but it is explained that the operation of this new machine depends simply upon hydraulic shear. In principle the mill consists of a conical seating in which a conical rotor revolves at a very high speed, the clearance between the two conical surfaces being very accurately adjustable.

If a mixture of a liquid and a solid can be passed into this machine, the action of the shearing forces due to viscosity as the liquid passes between the working surfaces serves to produce the desired effect. This machine has already received a number of important industrial applications, not merely for disintegration purposes, but for securing contact between immiscible liquids in the preparation of emulsions, and for similar work. The machine is very well constructed, and not too expensive.

The vacuum drying machinery used in this country is substantially unaltered in design since before the war. From time to time, however, suggestions come forward in connection with the condensing part of the operation, but in the past nothing has been found which would compete with the ordinary vacuum pump for the production of the vacuum.

Recently in this country there has been a tendency in power plants to employ steam ejectors for maintaining vacuum, and it is not surprising that the suggestion to apply these to vacuum drying and evaporating plants should arise. In the past the claims made by the makers of steam ejectors for vacuum production have been decidedly modest, and when one examines the figures given for steam consumption, and bears in mind the instability of such appliances against fluctuating duties, he is perhaps not surprised that the vacuum pump has always managed to hold its own.

An English firm has now commenced to manufacture a vacuum drying plant in which the vacuum is produced by a two-stage steam ejector of the Delas type, having water-jacketed diffusers. It is suggested that the exhaust steam from the ejector can be used for heating the vacuum drier, and it is stated that this system has been in use in France with excellent results.

This proposal is not new, for in the past similar schemes have been tried, but they have invariably been proved to be unreliable. In the case of the plant now under notice, it appears that the superiority claimed depends upon the use of the special type of ejector employed, and the statement has been published that, even though the steam supply to the ejector should fluctuate in pressure over very considerable limits, the performance is still satisfactory.

Much more interesting, however, is the experimental work which has been carried out by a large chemical firm in this country on the methods of producing vacuum in distilling plants for corrosive liquids. Some very excellent work in this direction has been done, using an apparatus very similar in principle to that of Siepermann. This apparatus is a sort of reversed air-lift pump in which the air is removed by means of a full tube something after the fashion of the Taylor hydraulic compressor.

This apparatus has no moving parts, and the working fluid in the pump may consist of the liquid which has to be finally condensed. The mechanical efficiency is not very high, but the wear and tear is negligible, and there is absolutely nothing to go wrong. It would not, however, be suitable for ordinary vacuum work, as the cost of running would be higher than that of ordinary vacuum pump, but where corrosive materials have to be handled the scheme seems to be very attractive.

#### COTTERILL PLANT INTERFERES WITH RADIO

A strange complaint has been heard from radio enthusiasts in the north of England. It appears that a certain Cotterill

dust-collecting plant creates a nuisance and effectually jams out broadcast wireless communications. It is understood that this matter is at present under investigation, but the plant in question emits the disturbance on a wave length of about 450 meters, with the result that tuning out is very difficult. This matter is rather interesting from a legal point of view, but it is difficult to believe that the trouble can be any worse than that created by electric trains, except that of course it will be continuous, and there can be no doubt that something will ultimately be done to abate the trouble.

September 14, 1923

## GERMAN LETTER

By WALTER ROTH, Götten, Germany

### TRAINING IN INDUSTRIAL CHEMISTRY

Recently in Germany there has been a revival of interest in the problem of training the chemist. During the war experience was the most important, so that in technical circles the necessary industrial education was lacking. Now, therefore, there comes more than ever the demand for the industrial point of view, the consideration of the economic aspects of the problem. A new branch of chemistry, industrial chemistry, will fill this gap in the education of the chemist, by training him along economic lines. For, today, in order to carry out a large chemical undertaking a mere knowledge of the subject is not sufficient; questions of procuring raw materials, or the possibilities for revenue of a process, and world economic problems must be solved, and for this a broader, industrially experienced point of view is needed.

### NEW MATERIALS FOR FUEL AND POWER

In the present fuel famine one naturally turns his attention to other sources of energy besides coal and lignite. But the "white coal" will for Germany, who is poor in water power, never be able to play a large part. Still less is to be expected of the "blue coal"—the using of the tide, by its ebb and flow—for German industry; and the large-scale utilization of the other forms of energy of earth and space—wind, sun, atmospheric electricity, etc.—are still in the distant future. Successful attempts have been made here and there to turn sewage and settling plants to purposes of light and power. For example, the City of Erfurt, in Thüringen, by experiments of the Erfurter Trichter Gesellschaft, has obtained out of a total quantity of 4000 cc. of mud, over 1,000,000 cc. of gas (marsh gas), and turned this to profitable use.

### DIRECT UTILIZATION OF RUBBER LATEX

It is well known that the milky juice of rubber, the so-called latex, is used directly, without first separating the rubber—for example, for the making of cord thread, of latex paper, etc. According to Ditmar it is suitable only where the latex can be given the form of the desired rubber article under simultaneous dehydration. When cement or plaster of Paris is used as the hardening agent, then vulcanization is not needed as these dehydrating agents act at the same time as vulcanizers. Through treatment with latex Ditmar will produce mothproof, elastic cushion and mattress fillings, since the loosened filling in the natural or pasteurized latex is wet and then left to dry off from the excess milky juice. The materials are thus covered with rubber, and therefore are mothproof, as rubber is not attacked by moths. This coating with rubber Ditmar calls "laxing," or after his own name, "ditmarizing." Ditmar will also use latex as a cementing material. He recommends latex glue, especially for the waterproof cementing of panes into windows.

### CHROMIUM INSTEAD OF NICKEL PLATING

The Electrochromgesellschaft, in Berlin, jointly with the Langbein-Pfanhauser Werken A. G., Leipzig, is using a new galvanic process by which coatings of chromium are made. Metallic chromium is separated electrolytically from chromium solutions in a form capable of being polished. These are platinum-colored, heat-resisting coatings, which are especially distinguished through their great hardness. They can be much thinner than nickel coatings, and are little attacked by the atmosphere, alkalies, acids, or salts. Especially can medical instruments, typewriter parts, phonograph plates, burners, lighters,

valves, etc., export articles with shining surfaces, which will not stand overseas transportation, be plated with chromium.

### DUST EXPLOSIONS

In mills, sugar factories, soap factories, etc., many dust explosions have been experienced without any one being able to find their cause. In sugar factories alone in the last thirty years almost seventy such explosions have taken place. In the Frankenthal plant the sugar chemist, Beyersdorfer, has been experimenting for a year and has found out that most explosions of this kind can be traced to electric causes. The dust explosions are to a certain extent "dust storms" by which the incipient lightning ignites the clouds of dust and causes them to explode. Beyersdorfer calls technical dust of this kind "colloid-chemical," and sees no difference between suspended dust, smoke, and clouds.

In this connection, he explains the rain of fire of Sodom and Gomorrah in a similar way. He says that with a violent outbreak of a petroleum well, perhaps in the Caucasus, followed by scattering and electrical charging of the liquid petroleum by the eruption out of a fissure in the earth, a petroleum cloud was formed. This cloud was then driven to Sodom and Gomorrah; there the oil was ignited by a flash of lightning and fell down as burning petroleum rain. Beyersdorfer rightly considered it fortunate that the particles of the clouds separated by the lightning in ordinary storms do not consist of combustible material; otherwise every storm would be a rain of fire.

For the prevention of dust explosions Beyersdorfer recommends limiting the formation of the dust as much as possible through the choice of appropriate disintegrating machines, not to grind too fine, to wet down the dust with water, and to remove the electrical charges through contact with the earth or through electrical neutralization.

### METHANE IN STEEL CONTAINERS

Methane from the Rombacher mines in Coblenz and from the Fritz Hamm Gesellschaft in Dusseldorf, compressed in the usual steel containers to 150 atmospheres, has recently been put on the market. This methane is entirely free from carbon monoxide, and is said to be generally useful as a cooking and lighting gas where a connection to a gas plant is not convenient or possible—as, for example, on ships, in remote villages, hamlets, and in factories situated far from the city. Methane light is pure white. Methane is suitable for soldering purposes, for the autogenic working of copper, brass, aluminium, and similar easily melted metals, as well as the autogenic cutting of iron. On account of its high calorific value and its extremely favorable kindling and compression points, methane is also useful as a material for gas motors, especially for vehicles. In the chemical use of methane, and therefore of natural gas, of which methane is the chief constituent, many prospects offer themselves. It is planned to obtain sulfur from gypsum by reduction with methane, to produce methanol from methane, with methyl chloride as an intermediate product, and from atmospheric nitrogen by the use of methane or its cleavage products to prepare cyanogen products. As is well known, methane decomposes at temperatures over 1000° C. into hydrogen and carbon. If, now, this very pure carbon is mixed with barium carbonate, or briquets are formed from the mixture, and these are heated in a stream of nitrogen at 1100° to 1300° C., barium cyanide is obtained. This new process of Prince Carl Löwenstein and Dr. Hauff makes possible the production of an air-nitrogen industry in the vicinity of natural gas sources.

August 23, 1923



## BOOK REVIEWS

**Surface Tension and Surface Energy and Their Influence on Chemical Phenomena.** By R. S. WILLOWS, M.A., D.Sc., and E. HATSCHK. 3rd edition, revised by R. S. WILLOWS. viii + 134 pages. 25 illustrations. P. Blakiston's Son & Co., Philadelphia, 1923. Price, \$2.00.

The owners of previous editions of this compact and convenient little treatise on a subject so closely connected with the important fields of colloid chemistry, adsorption, and catalysis will welcome this revised edition. The revision has consisted mainly in the enlargement of the text so as to include the recent work on the properties of thin films, surface solutions, boundary lubrication, and the relation between surface phenomena and the recent theories of molecular and atomic structure. Numerous other small additions and changes in other portions of the text have also been made to bring it up to date. The unnecessarily long and involved derivation of the Gibbs adsorption formula, given in the appendix, ought to be replaced by a shorter derivation of the rigorously exact equation which can be obtained directly from the Second Law. The assumptions necessary to convert the exact formula into the customary form can then be clearly brought out. These assumptions are not those indicated by the authors on p. 79, *et sec.*

E. W. WASHBURN

**Metals and Metallic Compounds.** By ULICK R. EVANS, M.A. 22.5 × 15 cm. Longmans, Green & Co., New York; Edward Arnold & Co., London, 1923. Vol. I, xii + 468 pages. Price \$7.00. Vol. II, xi + 396 pages. Price, \$6.00. Vol. III, xii + 270 pages. Price, \$4.75. Vol. IV, xii + 350 pages. Price, \$6.00.

This work is in reality an advanced text or handbook dealing with the chemistry of the metallic elements only. "The book is intended for the advanced student of inorganic and metallurgical chemistry and for those engaged in research in these subjects."

The first volume is of a general character and the first 120 pages are given to a presentation of the principles of general chemistry, physics, and geology. The contents of the main part of this volume is classified under two general headings, metallography and electrochemistry. The metallographic portion includes discussions of the structure of simple metals, the effects of deformation, and the effect of annealing and alloying on the properties of metals and the structure of alloys. Under the heading of electrochemistry are included chapters on such subjects as the structure of precipitates, the colloidal state, electrodeposition and corrosion, and electrolytic valve action. The volume is concluded with a chapter on radioactivity. This volume contains a wealth of material which should prove of interest to even the most advanced student of inorganic chemistry.

The remaining three volumes of the work are devoted to a consideration of the individual metals. Volume II deals with those elements classed as "A" groups, according to the periodic table of Sir James Walker, and includes the alkali and alkaline earth metals, aluminium and the rare earths, tantalum, columbium, and the chromium group. The space devoted to each metal is divided into three sections, the first dealing with the metal and its compounds, the second with the occurrence of the metal—including a discussion of its origin and formation of its compounds from the standpoint of geology, the third

dealing with the technology of the element or of such of its compounds as are of commercial importance.

Volume III deals with the transition elements—that is, the platinum and iron groups. The element iron is treated in a very comprehensive manner, 125 pages being devoted to it. The metallurgy of iron and the manufacture of common and alloy steels are presented in considerable detail.

Volume IV deals with the remaining metallic elements or the metals of the "B" groups, and includes arsenic and antimony.

In preparing this work the author has taken full advantage of the results obtained by research workers during the last few years to round out the presentation of the various subjects and bring the books up to date. As a result these books contain many subjects, presented in considerable detail, which are not now ordinarily found in books of this type. The books are unusually well written in a readable style and in the opinion of the reviewer are well worthy a careful perusal, particularly by advanced students or research workers in the fields of inorganic or metallurgical chemistry.

C. W. BALKE

**Industrial Filtration.** By ARTHUR WRIGHT. 336 pages. Chemical Catalog Co., Inc., New York. Price, \$5.00.

By definition of the title this book does not consider municipal water filtration, boiler water filtration, etc.

Part I, entitled "Theory of Filtration," might better be called "Art of Filtration," as no theoretical considerations as generally understood are made. It deals with clarification, cake, building, washing, discharging, filter media, theory (art?) of filter application and auxiliary equipment. It is fairly well written but lacks in specific information. Under "Cake Filtration" the methods used to determine the economical limit curve are questionable. The data are apparently not obtained by the best methods, and the conclusions are doubtful and certainly not applicable to the most commonly used filters. Under "Cake Washing" is given the usual misleading curve, which has appeared in print so many times, comparing simple washing in leaf filters with thorough washing in plate filters. If simple washing were used in both cases the curves would be quite alike. The impression is given that simple or displacement washing cannot readily be used in ordinary plate filters; whereas, as a matter of fact, it is used to a considerable extent. Thorough or alternate plate washing is a satisfactory method of washing, despite the author's impressions to the contrary. Under "Theory of Filter Application" the applications assigned to the five types are incomplete and hardly sufficient to effect a choice. "Auxiliary Equipment" is treated too briefly; it does not mention the montejus and gives too little attention to steam or power pumps or pump valves. There is nothing specific about the materials of which pumps should be made for use with various liquors.

Part II, "Mechanics of Filtration," might more understandably be called "Filtering Machines." Plate and frame filter presses are not handled well. Misstatements are made, producing a wrong impression of this most important filter of today. The rest of the section deals with suction, leaf, and vacuum filters. More space is devoted to these machines than their actual use in industry seems to warrant. A few other special filters of little importance are described. No description is given of the Berrigan, centrifugal, or pulp filters, although considerable space is given to thickeners, which are not filters at all.

Part III, "Filter Practice," gives general information of more or less value.

In general, the book contains a good description of the mechanics and operation of leaf or vacuum filters, and certain filtration ideas of value are advanced. Like many "technical" books, however, it lacks specific information. No cost data are given, and a list of the rates of flow of the common important substances is missing. Weights of various filters are also absent. The layout information is rather too brief and very few sketches appear. The average reader with a specific problem to solve would not be able to determine properly the type, size, or cost of filter to use from the information given.

It is unfortunate that the author mentions the names of certain manufacturers of equipment so frequently while names of others in the same line are not mentioned.

This book can be said to be equally as good as other books on this subject and represents an effort to produce a book which is much needed.

D. R. SPERRY

**The Chemical Engineering Catalog.** 8th Annual Edition. FRANCIS M. TURNER, JR., Technical Editor. 1049 pages, tables, diagrams, and illustrations. The Chemical Catalog Co., Inc., New York, 1923. Price, \$10.00. Leasing fee, \$2.00 (\$3.50 foreign).

So firmly established has the Chemical Engineering Catalog become as an institution in the chemical industries, that it would be almost unnecessary to comment on its annual appearance but for the fact that each succeeding edition shows plainly the result of the efforts being put forth by the supervising committee and the publishers to improve this standard reference work. In the earlier editions a great deal of material appeared which really partook more of the nature of advertising than of the type of data one might reasonably expect in a system of condensed catalogs. It was only natural that at first there should be a certain amount of confusion between this publication and various directories containing advertising that had appeared unofficially in other technical industries. However, year by year, more and more manufacturers of equipment have taken the trouble to study the requirements of those in charge of our chemical industries, and the present edition of the Chemical Engineering Catalog reflects this tendency.

It is particularly gratifying to note the much greater use of really explanatory diagrams and charts. There also seems to be an increase in the number of concerns giving detailed information as to sizes and capacities. There is still a dearth of information as to the costs of various equipment and materials. It would seem that approximate costs could be furnished in such a work where it is not possible to give exact figures.

The Equipment Section occupies the bulk of the book. The Chemicals and Materials Section is greatly improved and many of the larger manufacturers of chemicals are giving really detailed specifications of their products. However, there still remain in this section many pages which are mere lists of chemicals and other materials. Such pages certainly supply little information to prospective buyers, and in the case of a choice the business goes to the firm supplying the more detailed information.

A somewhat definite policy from previous years has been adopted with regard to the listings in the classified index at the front of the volume. Firms not cooperating in the catalog are now listed only in cases where they are not manufacturers of such products represented in the volume. This seems an entirely fair and satisfactory arrangement. It guarantees a complete reference work to the users of the catalog, and it relieves those who are cooperating in the support of the publication from the competition of firms contributing nothing to its support. Moreover, as the great majority of leading manufacturers are represented in the catalog, there are only relatively few instances where it is necessary to apply this rule.

The Technical and Scientific Book Section is considerably enlarged, and is interesting as being the only complete, up-to-date bibliography of technical books in English dealing with chemistry and closely allied subjects.

The quality of the paper and presswork seems to be even better than usual, and the general appearance of the volume conforms to the high standard established by previous editions.

**Chemische Technologie des Steinkohlenteers.** By R. WEISSGERBER. 141 pages. Otto Spamer, Leipzig, 1923. Price, \$1.50.

This monograph is a worthy member of the chemical technological series founded by Ferd. Fischer and edited by Arthur Binz. The subject matter, arranged in two main divisions, coking and coal tar, gives a concise and remarkably clear presentation of the most salient features, both theoretical and practical, of an industry in which the author is a recognized authority. The first division occupies thirty pages and deals with the various types of coal, their nature and probable formation, more particularly their behavior under destructive distillation in both low- and high-temperature operations, and the technic and chemistry of the resulting products. The remaining pages constitute the second division, coal tar, and deal with material derived exclusively from distillations at temperatures above 700° C. (high-temperature coking). Here the treatment is more elaborate, following the subdivisions: Theory of Tar Formation, Properties, Classification and Statistics, Tar Analysis, Transport and Storage, Tar Distillation, Light, Medium and Heavy Oils, Anthracene Oil, and Pitch. In addition to numerous references to pertinent literature, the book is well illustrated with up-to-date ovens, retorts, and apparatus peculiar to the industry, and is therefore well worth the attention of every progressive coal-tar technologist.

W. O. EMERY

**Betriebsverrechnung in der Chemischen Grossindustrie.** By ALBERT HEMPELMANN. vi + 107 pages. Julius Springer, Berlin, 1922. Price, \$1.15 unbound; \$1.40 bound.

Cost accounting in the chemical industry, with which this pamphlet deals, is of increasing importance to the works and managing chemist or engineer.

This work is comparatively brief and general in its treatment. It leans to the economist's or financial point of view rather than that of the production manager. The work is divided into six parts, with many sections and subdivisions. The main sections take up such subjects as the foundations of cost systems in the chemical industry, raw materials' cost, operating cost, calculation, calculation methods, detailed relation to various phases of management, critical discussion of the ideas presented and of practice.

The author recounts his own difficulty when he first entered this important field, through inability to locate help in the literature. He hopes to have aroused interest in the importance of the broader aspects of the subject, even if he may not always have succeeded in going into sufficient detail on the production side. The need seems to be recognized for separation from mere bookkeeping, to be not merely statistical, in order that cost accounting may be a proper scientific basis for policy building, independent of mere management.

Hempelmann clearly recognizes that in the necessities which arise in manufacturing, the demand for quick, ready information as to cost forces the cost accountant as well as the management into short-cut and make-shift methods which are of practical value for the time being, but which become so intricate that it is next to impossible to follow properly economic principles and detect false steps to the extent that is desirable.

The author thoroughly emphasizes at all times the simple fundamental relationships which determine cost of manufacture. He seems to be at home in the citation of illustrations from a variety of chemical industries. The work, however, has almost no diagrammatic or tabulated illustrations from actual experience and contains some apparent chemical blunders. For instance, on p. 88 "general theory" is stated to credit 1000 kg. of "salpeter" with the recovery of "7000 kg." of 100 per cent HNO<sub>3</sub>, whereas practice is credited with ability only to return a yield of 65 per cent against this "70 per cent."

The author calls attention to the fact that those who wish technical information as to how cost accounting should be carried out in particular industries in chemical business will naturally be disappointed in the sketchy character of his discussions. Nevertheless, the reviewer feels that any one interested in the philosophy of this problem will profit by a study of this contribution.

JAMES R. WITHROW

**Wärmewirtschaftsfragen. Monographien zur Feuerungstechnik, Heft 5.** By L. LITINSKY. 194 pages. Otto Spamer, Leipzig, 1923. Price, \$1.10.

This treatise on fuel economy in industrial works was written with a view of explaining the present practices in the saving of heat, and of adding something for increasing the scope of this important field. The book represents a revised and supplemented collection of a number of the author's own papers which have been published in various technical journals. Since most of these articles are now out of print, the material has been collected and presented in the form of a fairly unified book adapted to meet the needs of the practical fuel or heat engineer. The necessary theory and mathematics are presented in a very elementary manner, and the applications are illustrated by the use of many commercial examples.

The author has not attempted to cover here the entire field of industrial heat economy. In fact, one might say that the treatise concerns itself with problems of glass works, ceramic manufactures, and the devices used in connection with these industries, such as gas producers, regenerators, and furnaces.

The book is divided into eight parts, the first of which involves computations applicable to a gas-heated, kiln-burning refractory ware, and includes dimensions and characteristics of the oven, chimney, gas mains, and the producer-gas generator. Many other things, such as temperatures, efficiencies, fuel consumption, and products of combustion are also treated here.

The second topic, "Heat Balance Sheet of a Glass Smelting Oven," explains how the grate losses of the gas generator, the cooling of the gas in the mains, the radiation, conduction, and convection losses in the oven, and the latent heats of the by-products, are all balanced against the total calorific value of the fuel consumed and the reaction heats of the materials used in making the glass.

The third part gives very briefly the economic reasons for the manufacture of gas from wood and peat in certain localities. This is followed in the next part by a comparison of regenerators and recuperators, including typical heat balance sheets for each. The fifth section concerns itself with kinds of gas generators, applicability of low-grade fuels, determination of combustion temperatures, gas analyses, and important methods of economizing heat. Part Six, on the determination of the consumption of heat in the distillation of coal, brings in also the various methods of measuring gases, while the two remaining brief parts are on the determination of flue losses by analysis of the outgoing gases, and the comparison of the dry and wet methods of extinguishing coke.

G. R. GREENSLADE

## NEW BOOKS

- Advanced Practical Physics for Students.** B. L. WORSNOP AND H. T. FLINT. 640 pp. Price, \$8.00. E. P. Dutton & Co., New York.
- Aluminium Repairing.** WILLIAM H. H. PLATT. 77 pp. Illustrated. Price, \$1.50. D. Van Nostrand Co., New York.
- Annual Reports on the Progress of Chemistry for 1922.** Vol. XIX. THE CHEMICAL SOCIETY (LONDON). 321 pp. Price, \$3.00. D. Van Nostrand Co., New York.
- Applied Calculus. An Introductory Textbook.** F. F. P. VISCARE. 460 pp. Illustrated. Price, \$3.75. D. Van Nostrand Co., New York.
- Applied Optics. The Computation of Optical Systems.** ADOLPH STEINHEIL AND ERNEST VOIT. Translated and edited by JAMES WEIR FRENCH. Vol. I. 187 pp. Vol. II. 205 pp. Price, \$5.00 each, \$9.00 the set. D. Van Nostrand Co., New York.
- Atoms.** JEAN PERRIN. Translated by D. L. HAMMICK. 246 pp. Illustrated. Price, \$2.50. D. Van Nostrand Co., New York.
- Boy's Own Book of Science.** FLOYD L. DARROW. 331 pp. Price, \$2.50. The Macmillan Co., New York.
- Bureau Bulletin of the British Cast Iron Research Association.** No. 1. 102 pp. British Cast Iron Research Association, Birmingham.
- By-Product Coking.** G. STANLEY COOPER. 2nd edition. 192 pp. Price, \$4.50. D. Van Nostrand Co., New York.
- Civilization and the Microbe.** ARTHUR I. KENDALL. Price, \$2.50. Houghton Mifflin Co., Boston.
- Cotton Industry.** J. H. CRABTREE. 126 pp. Price, \$2.00. D. Van Nostrand Co., New York.
- Discovery, or The Spirit and Service of Science.** RICHARD GREGORY. American edition. 347 pp. Illustrated. Price, \$2.00. The Macmillan Co., New York.
- Elementary Steam Power Engineering.** EDGAR MACNAUGHTON. 590 pp. Illustrated. Price, \$5.00. John Wiley & Sons, Inc., New York.
- Everyday Mysteries. Secrets of Science in the Home.** CHARLES GREELEY ABBOT. Young People's Shelf of Science. 198 pp. Price, \$2.00. The Macmillan Co., New York.
- Fabrication du Vinaigre, d'après les Procédés les plus recents.** J. FRITSCH. 339 pp. Illustrated. Price, \$3.00. D. Van Nostrand Co., New York.
- Forge, Chaudronnerie, Ajustage.** M. HOVA. 132 pp. Price, 6 fr. Illustrated. Dunod, Paris.
- General Chemistry.** HORACE G. DEMING. 605 pp. Price, \$3.50. John Wiley & Sons, Inc., New York.
- Laboratory Directions in Inorganic Chemistry.** ALEXANDER SILVERMAN. 2nd edition, revised. Illustrated. Price, \$1.25. D. Van Nostrand Co., New York.
- Laboratory Experiments in Practical Physics to Accompany the Revised Edition of Black and Davis' "Practical Physics."** N. HENRY BLACK. 241 pp. Price, \$1.00. The Macmillan Co., New York.
- Laboratory Manual of Inorganic Chemistry.** JOHN B. EKRELEY. 2nd edition, revised. 225 pp. Price, \$1.50. John Wiley & Sons, Inc., New York.
- Manufacture of Lubricants, Shoe Polishes, and Leather Dressings.** RICHARD BRUNNER. Translated from the 6th German edition, 3rd edition, revised and enlarged. 252 pp. Price, \$4.00. D. Van Nostrand Co., New York.
- Mechanical Engineers' Handbook.** ROBERT T. KENT, Editor-in-Chief. 10th edition, rewritten and enlarged. 2247 pp. Illustrated. Price, \$7.00. John Wiley & Sons, Inc., New York.
- Modern Chemistry, Pure and Applied.** Vol. VI. ARTHUR J. HALE. 287 pp. Illustrated. Price, \$4.00. D. Van Nostrand Co., New York.
- Modern Gas Producers.** N. E. RAMBUSH. 545 pp. Price, \$15.00. D. Van Nostrand Co., New York.
- Oil and Gas Engine Power.** ALBERT W. DAW AND ZACHARIAS W. DAW. 468 pp. Illustrated. Price, 45 s. net. Constable & Co., London.
- Outline for Qualitative Analysis.** HERBERT O. SMITH. 4 pp. Price, \$0.10. D. Van Nostrand Co., New York.
- Outlook for Research and Invention.** NEVIL MONROE HOPKINS. 256 pp. Price, \$2.00. D. Van Nostrand Co., New York.
- Petroleum Resources of the World.** VALENTIN R. GARFAS. 243 pp. Illustrated. Price, \$3.00. John Wiley & Sons, Inc., New York.
- Practical Optics.** B. K. JOHNSON. 189 pp. Price, \$3.75. D. Van Nostrand Co., New York.
- Practical Polishing and Staining.** A. W. PARKHOUSE. 128 pp. Price, \$3.00. D. Van Nostrand Co., New York.
- Structural Design in Theory and Practice.** HENRY ADAMS. 2nd edition. 265 pp. Price, \$3.50. D. Van Nostrand Co., New York.
- Systematic Inorganic Chemistry. From the Standpoint of the Periodic Law.** R. M. CAVEN AND G. D. LANDER. New edition. 478 pp. Price, \$3.00. D. Van Nostrand Co., New York.
- Textbook of Intermediate Physics.** H. MOORE. 824 pp. Price, \$9.00. E. P. Dutton & Co., New York.
- Treatment of Paper for Special Purposes.** LOUIS EDGAR ANDÉS. Translated from the German. 2nd English edition, revised and enlarged. 216 pp. Price, \$3.50. D. Van Nostrand Co., New York.



# MANUFACTURERS' TECHNICAL PUBLICATIONS

**Notice**—Any publications mentioned under this heading will be sent free, unless otherwise noted, to readers of *This Journal*, on request to the firm issuing the publication. When writing for any of these items kindly mention *Industrial and Engineering Chemistry*.

**Abbé Specialties.** Catalogs A, B, C, E, G, H, covering crushing, cutting, grinding, mixing, pulverizing, and sifting machinery. 8 to 32 pp. PAUL O. ABBÉ, INC., 73 Murray St., New York, N. Y.

**Acimet Valve.** Catalog showing patterns, sizes, and prices of corrosion-resistant valves. 24 pp. CLEVELAND BRASS MFG. CO., 4606 Hamilton Ave., N. E., Cleveland, Ohio.

**Barnstead Water Still.** General catalog showing uses and applications of this apparatus, with specifications and tables. 34 pp. BARNSTEAD STILL & STERILIZER CO., INC., Boston, Mass.

**Beach-Russ Rotary Pumps.** *Bulletin 32*, illustrating and describing this equipment. 8 pp. BEACH-RUSS CO., 50 Church St., New York, N. Y.

**Brown Electrical Indicating and Recording CO<sub>2</sub> Meters.** *Catalog 30*. Contains diagrams, illustrations, and instructions concerning application and use of these meters. 8 pp. BROWN INSTRUMENT CO., Philadelphia, Pa.

**Buflovak Apparatus for Producing Dry and Evaporated Milk Products.** New booklet showing applications of this equipment, with useful data and tables. 36 pp. BUFFALO FOUNDRY & MACHINE CO., 1549 Fillmore Ave., Buffalo, N. Y.

**California Redwood.** Brochure giving interesting and instructive information in regard to general and industrial uses of this material. 36 pp. PACIFIC LUMBER CO., McCormick Bldg., Chicago, Ill.

**Chemical and Metallurgical Laboratory Supplies.** *General Catalog AA*, showing complete line of such equipment and supplies with illustrations, specifications, and prices. Cloth. 606 pp. EIMER & AMEND, Third Ave., 18th to 19th Sts., New York, N. Y.

**Chemical Equipment of Metal.** Catalog illustrating and describing Bethlehem apparatus. 48 pp. BETHLEHEM FOUNDRY & MACHINE CORP., Room 1716, Grand Central Terminal, New York, N. Y.

**Chemicals and Drugs.** 206 pp. EIMER & AMEND, New York, N. Y.

**Christie Dryers, Calciners, Coolers.** Illustrated treatise covering the design and application of such equipment for the chemical industries, with data and charts of special interest to the chemical engineer. 16 pp. L. R. CHRISTIE CO., 307 Fourth Ave., Pittsburgh, Pa.

**CO<sub>2</sub> Recorder Accessories.** *Bulletin 116-A*, describing three new accessories in this line designed to reduce operating attention. 8 pp. UEHLING INSTRUMENT CO., 473 Getty Ave., Paterson, N. J.

**Current Duriron Literature.** Bulletin revised to September, 1923, giving complete data and tables on uses and applications of Duriron corrosion-resistant metal. 48 pp. Loose-leaf with binder. DURIRON CO., Dayton, Ohio.

**Data concerning Platinum.** General catalog covering the subject, with tables and sizes, capacities, and weights. 88 pp. BAKER & CO., INC., Murray and Austin Sts., Newark, N. J.

**Dopp Equipment.** *Catalog VII*, describing seamless-jacketed kettles, mixers, vacuum and pressure apparatus. 64 pp. SOWERS MANUFACTURING CO., Buffalo, N. Y.

**Duriron Acid-Proof Drain Pipe.** 24 pp. DURIRON CO., Dayton, Ohio.

**Electric Furnaces for the Laboratory.** 22 pp. NORTON CO., Worcester, Mass.

**Electrical Instruments for Ion Concentration Measurements.** BROWN INSTRUMENT CO., Philadelphia, Pa.

**Elementary Photographic Chemistry.** A technical treatise on this subject, containing much valuable information and precise data of interest to those engaged in this special field. 80 pp. EASTMAN KODAK CO., Rochester, N. Y.

**Elyria Glass Enameled Equipment.** *Bulletin 31*. Technical treatise on glass-enameled ware for the chemical, pharmaceutical, and allied industries. 20 pp. THE ELYRIA ENAMELED PRODUCTS CO., Elyria, Ohio.

**Engelhard Equipment.** Series of bulletins in loose-leaf binder, covering impervite porcelain and refractories, LeChatelier pyrometers, electric thermometers, electric furnaces, and quartz glass. CHARLES ENGELHARD, INC., 30 Church St., New York, N. Y.

**Hard Rubber Chemical Equipment.** Bulletins on hard rubber pumps, pipe, fittings and utensils. Loose-leaf with binder. AMERICAN HARD RUBBER CO., 11 Mercer St., New York, N. Y.

**Hartman Sterilizers.** A series of bulletins in loose-leaf binder, describing, with illustrations and charts, this electrolytic water-purifying apparatus. 24 pp. UNITED STATES OZONE CO., Scottsdale, Pa.

**Heusser Precision Balances.** *Bulletin 65*, containing tables of dimensions and weights, with illustrations. 24 pp. THE MINE & SMELTER SUPPLY CO., P. O. Box 119, Denver, Colo.

**Kewaunee Book of Laboratory Furniture.** New edition. General catalog covering complete line of this manufacturer. Cloth. 408 pp. KEWAUNEE MFG. CO., Kewaunee, Wis.

**Knight Chemical Stoneware.** General catalog fully describing and illustrating this apparatus, with comprehensive data and illustrations. 54 pp. MAURICE A. KNIGHT, Kelly Ave., East Akron, Ohio.

**Koerting Condensers and Recooling Systems.** Group of bulletins in loose-leaf binder covering multi-jet condensers, atmospheric heating valves, high-vacuum, air-jet oil pumps, recooling nozzles, vacuum traps, oil separators, etc. 60 pp. SCHUTTE & KOERTING CO., 12th and Thompson Sts., Philadelphia, Pa.

**Material of a Thousand Uses.** Brochure, illustrated in color, describing the uses and applications of the phenol condensation products, Bakelite, Condensite, and Redmanol. 24 pp. BAKELITE CORP., 8 West 40th St., New York, N. Y.

**Norton Refractories, Alundum-Crystolon.** Fused alumina refractories and laboratory ware. Catalog. 64 pp. NORTON CO., Worcester, Mass.

**Physical Apparatus and General Laboratory Supplies.** *Catalog H-D*. 1923. 106 pp. WM. GAERTNER & CO., 5345 Lake Park Ave., Chicago, Ill.

**Potentiometer Pyrometers.** *Catalog 87*, containing comprehensive and valuable data and charts in regard to pyrometer practice. 44 pp. LEEDS & NORTHRUP CO., 4901 Stenton Ave., Philadelphia, Pa.

**Proctor Dryers for Cotton.** Illustrated handbook covering application of drying equipment for cotton. Fully illustrated. 32 pp. PROCTOR & SCHWARTZ, INC., Philadelphia, Pa. (Also published by same firm: Proctor Dryers for Hair, Leather, Silk Piece Goods, Knit Goods and Cloth; Proctor Dryers for Yarn.)

**Pulverizing, Grinding, and Mixing Machinery.** *Bulletin 20*, giving technical data on this subject, with tabular matter and illustrations. 12 pp. ABBÉ ENGINEERING CO., 50 Church St., New York, N. Y.

**"Scientia" and "Studentia" Calorimeters.** *Catalog C*. 34 pp. WM. GAERTNER & CO., 5345 Lake Park Ave., Chicago, Ill.

**Sharples Super Centrifuges.** Illustrated bulletin on commercial applications of this type of equipment. Diagrams and complete exposition, list of processes successfully employing the super-centrifugal systems. 24 pp. THE SHARPLES SPECIALTY CO., 23rd and Westmoreland Sts., Philadelphia, Pa.

**Sperry Filter Press.** *Catalog 14*, containing illustrations, charts, and technical data on the use and application of filter press equipment of special interest to the chemical engineer. 60 pp. D. R. SPERRY & CO., Batavia, Ill.

**Standard Laboratory Apparatus.** Adopted by the Manufacturing Chemists Association of the United States. 50 pp. EIMER & AMEND, New York, N. Y.

**Stokes Pharmaceutical and Chemical Apparatus.** General catalog with complete data and illustrations. 100 pp. F. J. STOKES MACHINE CO., Cedar Grove Station, Philadelphia, Pa.

**Swenson Evaporators.** *Technical Bulletin E-122*. Illustrated. 16 pp. SWENSON EVAPORATOR CO., Harvey, Ill.

**The Truth about Ozone.** 64 pp. UNITED STATES OZONE CO., Scottsdale, Pa.

**Vertical Cylindrical Electric Furnaces.** *Instruction Book 88,712*. Loose-leaf bulletin with illustrations, diagrams, and much technical data on electric furnaces for various uses. 26 pp. GENERAL ELECTRIC CO., Schenectady, N. Y.

**Vitreosil Data.** Technical booklet giving useful data, tables, and prices on fused silica ware. 16 pp. THERMAL SYNDICATE, LTD., 350 Madison Ave., New York, N. Y.

## Spring Meeting Reservations

Members planning to attend the spring meeting of the SOCIETY, which will be held in Washington, D. C., during the week of April 21, 1924, should make their reservations now. The meeting will be held at the time when the hotels will be overcrowded, and in order to be sure of good accommodations reservations should be made immediately. The New Willard has been chosen as hotel headquarters, but if you do not desire to write to the hotel directly requests for reservations may be sent to H. C. Fuller, chairman of the Committee on Hotels and Transportation, Institute of Industrial Research, 1845 B Street, N. W., Washington, D. C.

# GOVERNMENT PUBLICATIONS

## Commerce Reports—September

**Notice**—Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is \$3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.

A national gas exhibition was held at Bingley Hall, Birmingham, England, from September 17 to October 3, 1923, for the purpose of demonstrating and further popularizing the service and use of gas in home and industry. (P. 612)

Producers of china clay are much interested in experiments that are being conducted on the use of fuel oil in drying their product in Cornwall and Devon. A six months' test has demonstrated a considerable saving over coal and that fuel-oil plants are adapted to existing kilns and furnaces. (P. 621)

Recent regulations of the Polish government provide that producers of crude oil must declare to the State oil bureau on or before the 15th of each month their gross production for the preceding month. The State oil bureau, in turn, shall signify before the 10th of the month whether they will purchase the oil produced during the preceding month. If the State oil bureau does not indicate a desire for the oil then it is available for the general market. (P. 621)

There is a fair market for disinfectants in Hongkong and a growing demand for sanitary disinfectants in the Canton consular district. (Pp. 629-30)

The coefficient of increase of 2.5, by which the basic import duties on crude iodine have been multiplied since December 2, 1922, has been removed by a French law. (P. 638)

New processes have resulted in the extraction of crude rubber in North Central Mexico containing less than one-half of 1 per cent of water, and it is possible that there may be a revival of the industry which formerly brought considerable wealth to this district. (P. 650)

The Mexican government has under consideration a project for the encouragement of the use of oil for household fuel and cooking purposes as a part of its campaign to conserve the forest resources of Mexico. (P. 671)

The growth of the Peruvian fuel oil trade during the past three years is quite notable. An important development is the recent substitution of the native oil in place of coke in the largest smelter of the republic. (P. 672)

The new substitute for gasoline, called "Dynaalkol" was recently tested in a number of flights made by the Czechoslovak Aviation Service, and has proved to be even more efficient than gasoline. The Czechoslovak government is planning exhaustive tests with this new fuel. (P. 672)

The foreign trade of the United States in chemicals and allied products for the month of July, 1923, as compared with the corresponding month of last year, showed an expansion of 48 per cent in exports. (P. 676)

The German chemical industry in the first half of 1923 is reviewed. (Pp. 677-8)

During 1922 the asbestos sold and shipped from the mines of Quebec amounted to 160,339 tons, as compared with 87,475 tons in 1921. (Pp. 680-1)

Recent press items report the appointment of a Canadian commission consisting of five members, to inquire into the forest resources of Canada and to determine the necessity for placing an embargo upon the exportation of pulpwood from Canada. (P. 717)

It is expected that a bill will be introduced in the Australian parliament abolishing the import duty on sulfur and granting a bounty to domestic producers of sulfur. (P. 718)

Certain changes in patent, design, and trade-mark law of Germany are cited. (P. 719)

A royal decree of Greece extends the time during which the requirements of the patent law with respect to working the invention and paying the fees may be complied with and forfeiture of the patent avoided. (P. 719)

The situation in heavy chemicals in France in August was calm, with little change in prices. Secondary chemicals were relatively active, tannery stocks were small, the dye situation was calm, and there was slack demand for paint-making materials. (P. 724)

At a recent conference of the Sugar Club in Havana it was decided that hereafter the standard temperature for graduation

of Brix hydrometers for the laboratories exchanging information under the club agreement shall be 17.5° C. (P. 731)

According to a review of the Mexican paint situation, Mexico presents a good field for the sale of American paints, and it is pointed out that unsuccessful bids may lead to future business. (Pp. 732-3)

Netherlands India, which admits chemical fertilizers free of duty, offers a good field for the American product. (Pp. 733-4)

The French occupation of the Ruhr Valley has had no apparent effect on the chemical and dye trade of Germany in Mexico. The prices of German dyes and chemicals in Mexico have not increased and representatives of American manufacturers of dyes and chemicals report that they can note no increase in orders since the occupation of the Ruhr. (P. 734)

There is a good demand for paints in Mexico City. White lead and paste ground in oil meet an especially ready sale, although throughout most of Mexico water paints are in greater demand. (Pp. 735-6)

A portion of the coast of Lower California is the source of a small quantity of seaweed, which is processed for the production of vegetable gelatin or agar-agar. (P. 736)

The original French text and a translation or summary in English of the various French decrees relating to the compulsory purchase of industrial alcohol by importers of gasoline is on file in the Petroleum Division of the Bureau of Foreign and Domestic Commerce and may be consulted by interested parties. (P. 741)

Greek import duties have been modified on paraffin wax, ceresin, and all mineral wax not specified; on naphthalene, monosulfide, sulfate, hyposulfide, hypochloride of soda, chloride of lime, and chloride of magnesium; and on celluloid, gluten, casein, imitation amber, and similar materials. (P. 765)

Changes have been made in the Argentine export duty on linseed. (P. 766)

The duty on heavy oils, residues of petroleum, and other mineral oils imported into St. Pierre and Miquelon, France, has been reduced from 6 francs to 0.10 franc per 100 kilos. (P. 767)

The Chilean nitrate industry has succeeded in working itself out of a very critical position and is once more on a stable basis. The great prosperity in the metal trades in the United States has also resulted in a greatly increased demand for Chilean copper, Chile's second important export staple. (P. 778)

The crude rubber survey authorized by Congress and undertaken by the Department of Commerce is now under way in every region where investigations were originally planned. After the return of the parties composing the various expeditions to Washington their separate findings will be assembled in the form of a complete report. (Pp. 800-1)

The effect of monopoly on the camphor industry and trade is described, and it is pointed out that the restrictions of the Japanese monopoly have resulted in various countries encouraging the domestic production of natural camphor and have also stimulated efforts to solve the problem of the profitable manufacture of synthetic camphor. (Pp. 808-11)

The production of crude mineral oil in France decreased 50 per cent for the second quarter of 1923. (P. 819)

A decree by the Polish Ministers of Finance and Industry and Commerce provides for a reduction of certain duty coefficients on fertilizers, certain chemical products, and oils for the manufacture of margarine and other edible fats. (P. 833)

The production in Soviet Russia of all the basic chemicals, as well as fertilizer, showed a steady increase during the first half of 1923. Production statistics are given for these chemicals divided into three groups—acids, alkalies, and salts. (P. 841)

### STATISTICS OF EXPORTS TO THE UNITED STATES

Curacao—(P. 620)	Japan—(Pp. 734 and 771)
Crude oil	Agar agar
Shanghai—(P. 649)	Camphor
Antimony	Canada—(P. 742)
Camphor, crude	Pulpwood
Wood oil, Chinese	Austria—(P. 744)
Constantinople—(P. 711)	Magnesite
Licorice root	Africa—(P. 781)
Manganese ore	Bliester copper
Opium	Chrome ore
Hongkong—(P. 735)	
Anise oil	

### SPECIAL SUPPLEMENTS ISSUED

Petroleum in Foreign Trade and Services of the Petroleum Division.  
The German Coal-Tar Chemical Industry: Production, Export, and Import Statistics. *Trade Information Bulletin* 141.

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

- Anthracite Substitutes. O. P. HOOD. *Reports of Investigations* 2519. 4 pp. Issued August, 1923.
- Comparative Engine Tests with Crude, Acid-Refined, and Silica-Gel Refined Motor-Benzol. A. C. FIELDNER AND G. W. JONES. *Reports of Investigations* 2517. 3 pp. Issued August, 1923.
- Effect of Cooling Systems on Evaporation Losses of Gasoline. LUDWIG SCHMIDT. *Reports of Investigations* 2531. 12 pp. Issued September, 1923.
- Eighth Semiannual Motor Gasoline Survey. N. F. LEJEUNE AND H. M. SMITH. *Reports of Investigations* 2525. 3 pp. Issued September, 1923.
- Forms of Sulfur in Steamed Coke and Their Action in the Blast Furnace. J. H. THOMPSON. *Reports of Investigations* 2518. 7 pp. Issued August, 1923.
- Fuels Available for Domestic Use as Substitutes for Anthracite Coal. RUDOLF KUDLICH. *Reports of Investigations* 2520. 7 pp. Issued August, 1923.
- Leaching Nonsulfide Copper Ores with Sulfur Dioxide. C. E. VAN BARNEVELD AND E. S. LEAVER. *Technical Paper* 312. 91 pp. Paper, 20 cents.
- Oxygen-Oil Explosions. Preliminary Report II. Spontaneous Ignition of Metals in Oxygen under Pressure. J. J. JAKOWSKY AND E. W. BUTZLER. *Reports of Investigations* 2521. 4 pp. Issued September, 1923.
- Preparation and Detonating Properties of Cyanuric Triazide. C. A. TAYLOR AND W. H. RINKENBACH. *Reports of Investigations* 2513. 4 pp. Issued August, 1923.
- Progress in Blast-Furnace Research. P. H. ROYSTER, T. L. JOSEPH, AND S. P. KINNEY. *Reports of Investigations* 2524. 6 pp. Issued September, 1923.
- Strength and Sensitiveness of TNT as Determined by the Laboratory "Sand-Test" Bomb. C. A. TAYLOR AND R. D. LEITCH. *Reports of Investigations* 2526. 5 pp. Issued September, 1923.
- Survey of Pacific Coast Petroleum Products. Part III. Burning and Fuel Oils. E. C. LANE AND N. F. LEJEUNE. *Reports of Investigations* 2511. 11 pp. Issued August, 1923.
- Tests of a Powdered-Coal Plant. A Report of Investigations at the Power Plant of the St. Joseph Lead Co., Rivermines, Mo. HENRY KREISINGER, JOHN BLIZARD, C. E. AUGUSTINE, AND B. J. CROSS. *Technical Paper* 316. 22 pp. Paper, 5 cents.
- The Electrothermic Metallurgy of Zinc. B. M. O'HARA. *Bulletin* 208. 106 pp. Paper, 15 cents. This bulletin represents work done under a cooperative agreement between the Bureau of Mines, Department of the Interior, and the Missouri School of Mines and Metallurgy.
- The Use of Highly Volatile Natural-Gas Gasoline as a Refrigerant. L. D. WYANT. *Reports of Investigations* 2510. 10 pp. Issued August, 1923.
- Water-Gas Tar Emulsions. W. W. ODELL. *Technical Paper* 304. 51 pp. Paper, 10 cents. This paper represents work done under a cooperative agreement between the Bureau of Mines, Department of the Interior, the State Geological Survey Division of the State of Illinois, and the Engineering Experiment Station of the University of Illinois.

### Bureau of Fisheries

- Northwestern Lakes of the United States: Biological and Chemical Studies with Reference to Possibilities in Production of Fish. GEORGE KEMMERER, J. F. BOVARD, AND W. R. BOORMAN. *Document* 944. 92 pp. Paper, 25 cents.

### Bureau of Foreign and Domestic Commerce

- A World Resumé of the Paint Situation with Statistical Tables Showing Complete Exports from the United States for 1922. *Special Circular* 9, Chemical Division. 24 pp.

### Bureau of the Census

- Essential Oils. Census of Manufactures, 1921. 8 pp. Paper, 5 cents.
- Explosives. Census of Manufactures, 1921. 10 pp. Paper, 5 cents.
- Paper and Wood Pulp. Census of Manufactures, 1921. 17 pp. Paper, 5 cents.
- Salt. Census of Manufactures, 1921. 7 pp. Paper, 5 cents.

### Department of Agriculture

- An Improved Method for the Determination of Nicotine in Tobacco and Tobacco Extracts. O. M. SHEDD. *Journal of Agricultural Research*, 24 (June 16, 1923), 961-70.

- A Study of Factors Affecting the Nitrogen Content of Wheat and of the Changes That Occur during the Development of Wheat. G. A. OLSON. *Journal of Agricultural Research*, 24 (June 16, 1923), 939-53.
- Apple By-Products as Stock Foods. G. P. WALTON AND G. L. BIDWELL. *Department Bulletin* 1166. 40 pp. Issued July 26, 1923. Paper, 5 cents.
- Effect of Different Concentrations of Manganese Sulfate on the Growth of Plants in Acid and Neutral Soils and the Necessity of Manganese as a Plant Nutrient. J. S. MCHARGUE. *Journal of Agricultural Research*, 24, (June 2, 1923), 781-94.
- Efficiencies of Phosphatic Fertilizers as Affected by Liming and by the Length of Time the Phosphates Remained in Porto Rican Soils. P. L. GILE AND J. O. CARRERO. *Journal of Agricultural Research*, 25 (July 28, 1923), 171-95.
- Growth-Promoting Value of the Proteins of the Palm Kernel, and the Vitamin Content of Palm-Kernel Meal. A. J. FINKS AND D. B. JONES. *Journal of Agricultural Research*, 25 (July 28, 1923), 165-9.
- Nutritive Value of Mixtures of Proteins from Corn and Various Concentrates. D. B. JONES, A. J. FINKS, AND C. O. JOHNS. *Journal of Agricultural Research*, 24 (June 16, 1923), 971-8.

### Geological Survey

- Arsenic in 1922. V. C. HEIKES AND G. F. LOUGHLIN. Separate from Mineral Resources of the United States, 1922, Part I. 24 pp. Published September 17, 1923.
- Clay in 1922. JEFFERSON MIDDLETON. Separate from Mineral Resources of the United States, 1922, Part II. 8 pp. Published October 10, 1923.
- Fuller's Earth in 1922. JEFFERSON MIDDLETON. Separate from Mineral Resources of the United States, 1922, Part II. 3 pp. Published September 15, 1923.
- Magnesium and Its Compounds in 1922. J. M. HILL AND G. F. LOUGHLIN. Separate from Mineral Resources of the United States, 1922, Part II. 17 pp. Published September 20, 1923.
- Mineral Resources of the United States, 1921. Part I—Metals. G. F. LOUGHLIN. 766 pp. Price, \$1.00. A consolidation of reports on the different metals published separately between May, 1921, and July, 1922, with a summary covering both metals and nonmetals.
- Quicksilver in 1922. F. L. RANSOME. With a Supplementary Bibliography. I. P. EVANS. Separate from Mineral Resources of the United States, 1922, Part I. 12 pp. Published September 18, 1923.
- Strontium in 1922. G. W. STROSE. Separate from Mineral Resources of the United States, 1922, Part II. 3 pp. Published September 12, 1923.
- Surface Water Supply of Hawaii July 1, 1918, to June 30, 1919. N. C. GROVER, C. T. BAILEY, AND J. E. STEWART. *Water-Supply Paper* 515. 123 pp. Paper, 15 cents. Prepared in cooperation with the Territory of Hawaii.
- Surface Water Supply of the United States 1919-1920. Part VI—Missouri River Basin. N. C. GROVER, W. A. LAMB, ROBERT FOLLANSBEE, W. G. HOYT, AND R. C. RICE. *Water-Supply Paper* 506. Prepared in cooperation with the States of Montana, Wyoming, Iowa, Colorado, and Kansas. 411 pp. Paper, 35 cents.
- The Twenty-Mile Park District of the Yampa Coal Field, Routt County, Colorado. M. R. CAMPBELL. *Bulletin* 748. 82 pp. Paper, 20 cents.
- Tin in 1922. B. L. JOHNSON. Separate from Mineral Resources of the United States, 1922, Part I. 4 pp. Published October 11, 1923.

### Public Health Service

- Collection and Preservation of Blood Samples for Determination of Carbon Monoxide. R. R. SAYERS, H. R. O'BRIEN, G. W. JONES, AND W. P. YANT. *Public Health Reports*, 38 (August 31, 1923), 2005-11.
- On the Composition of the Precipitate from Partially Alkalinized Alum Solutions. L. B. MILLER. *Public Health Reports*, 38 (August 31, 1923), 1995-2004.
- Public Health Service Publications. A List of Publications Issued between October, 1922, and April, 1923. *Reprint* 338 from *Public Health Reports* 4 pp.
- Sewage Treatment in the United States. Report on the Study of Fifteen Representative Sewage Treatment Plants. H. H. WAGENHALS AND OTHERS. *Public Health Bulletin* 132. Price, 50 cents.
- State Laws and Regulations Pertaining to Public Health, 1920. JASON WATERMAN AND OTHERS. *Supplement* 43 to *Public Health Reports*. Paper, 25 cents.
- The Elimination of Carbon Monoxide from Blood, by Treatment with Air, with Oxygen, and with a Mixture of Carbon Dioxide and Oxygen. R. R. SAYERS AND W. P. YANT. *Public Health Reports* 38 (September 7, 1923), 2053-74.

### Tariff Commission

- Census of Dyes and Other Synthetic Organic Chemicals, 1922. *Tariff Information Series* 31. 185 pp. Paper, 20 cents.

# MARKET REPORT—OCTOBER, 1923

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

WHILE the volume of business during the month has been showing a steady increase over that of the preceding month, the total volume has not been up to expectations of leading interests in industrial chemicals. Demand has been spotty for the greater part of the period, but with the approach of the season for making contracts for the coming year buying is expected to become steadier. Consuming industries have been slow in recovering from the usual summer depression. Textile mills, especially in New England, have been showing little increased activity and several mills have announced curtailment of operations from half-time to closing for indefinite periods. Continued warm weather for the season of the year has also had its effect upon buying in general.

Although there has been no general announcement in alkali prices, it is understood that other manufacturers will maintain their former selling prices for contracts for the coming year similar to those recently announced by one manufacturer. Demand for alkalies has been increasing steadily but prices have shown no change or fluctuation in over two years. Cost of production has increased, but the increased consumption has offset to some extent the difference in operation advances. Bleaching powder has been subject to much price-cutting during the summer and early fall. Keen competition and a slackening demand has caused sellers to disregard formal and open prices for their own private terms wherever business has been available. Sales have been reported as low as  $1\frac{1}{8}$  cents per pound at the works.

On the first of the month a reduction in the price of bleach for the last quarter from \$1.75 to \$1.65 was announced by a leading maker. Continued weakness in the market, however, forced another reduction on the 15th to \$1.25 for October delivery, and \$1.50 for November and December. Contract prices for the coming year were also announced for chlorine and bleaching powder. Contract prices for next year have been announced by a leading maker of bichromates and they are the same as those which ruled during 1923. One maker of bichromates has reduced sodium bichromate to  $7\frac{1}{8}$  cents a pound for car-lot quantities, which is considerably under the announced contract prices. Competition for bichromate business has been very keen. Heavy acids have been moving fairly well, with sulfuric acid in greatest demand. Formic acid has been active and supplies are stated to be small in the face of present demand. Lactic acid continues in steady demand.

Arsenic has been receiving more attention recently and prices have advanced owing to more active demand and a scarcity of supplies in the market. Japan has not been offering arsenic during the past month and German import prices are above domestic and local prices. Domestic producers are understood to have little to offer. Recent lack of demand for copper and

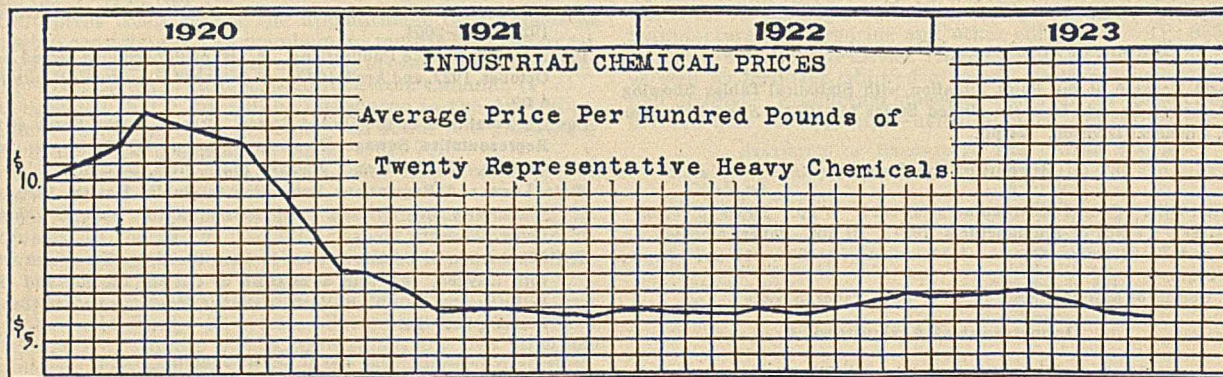
slowing up of smelters may have some effect upon the domestic output of arsenic, since it is a by-product of the copper smelters. The season for calcium arsenate is over and makers are beginning to prepare for next season. Ammonium chloride is stronger and higher in price. Barium products have been strong, especially the carbonate, domestic makers being well sold ahead and imported material difficult to obtain. Barium chloride is firm and shipments from abroad are higher. Acetone continues in limited supply. Copper sulfate has been declining slightly with the drop in metallic copper prices.

Domestic caustic potash has been reduced to the level quoted by importers of German potash. Potassium chlorate is firm at recent levels. Prussiates have shown no improvement in demand and prices are lower for both sodium and potassium prussiates. Demand for colors made from prussiates has been lacking, and sellers have been forced to reduce prices in order to move their stocks. Imported potassium permanganate is higher at  $17\frac{3}{4}$  cents per pound while domestic material is unchanged at 17 cents at works. Soda ash and caustic soda continue in steady demand. Export demand for caustic soda has shown a slight improvement. Sodium sulfide is beginning to improve after a dull summer. Glauber's salt is in slightly better demand at unchanged prices. Formaldehyde is easier on accumulation of stocks and small demand.

Crude coal-tar products have been showing steady decline in prices. Benzene and toluene are lower owing to an accumulation of stocks and the lower market in gasoline in competition with which 90 per cent benzene is sold. Demand has been spotty and buyers are not inclined to anticipate their requirements for the future. Solvent naphtha and xylene are slightly lower. Phenol had been holding fairly steady until about the middle of the month when one seller announced a reduction to 26 cents a pound, a decline of 2 cents a pound below previous levels. Cresylic acid has been fairly active with prices at former levels. Pyridine is very scarce and prices have advanced to \$6.00 and above for material on spot. Shipments are difficult to obtain from abroad and domestic production is insufficient for present needs.

Intermediates have been moving slowly owing to the poor demand for colors. The situation is controlled by manufacturers, however, and little is being produced except as required for routine consumption. Prices have remained steady during the dull period, except for occasional lots in the resale market. With increased demand prices will probably become firmer, but no sharp advances are expected. Salicylates have been steady in price and demand with the statistical position firm. Medicinal chemicals have been moving in a seasonal way.

Vegetable, animal, and fish oils have been more active and prices have shown an upward trend. Linseed oil is higher, though the demand is mainly routine in character.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

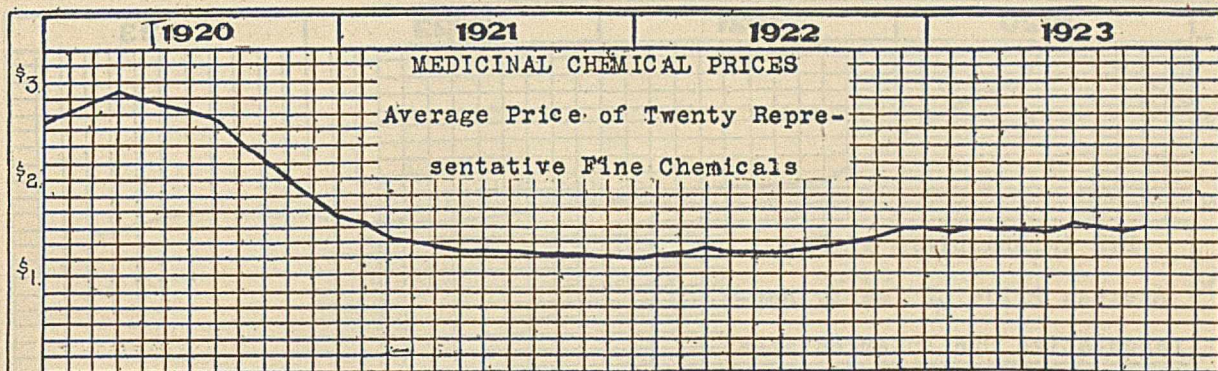
	Oct. 1	Oct. 15	Jan. 1923
Acid, Boric, cryst. bbls.....lb.	.11	.11	.11½
Hydrochloric, comm'l. 20° lb.	.01½	.01½	.01½
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.73	.73	.65
Nitric, 42° cbys. c/1 wks.lb.	.06½	.06½	.06
Phosphoric, 50% tech...lb.	.08	.08	.08
Sulfuric, C. P.....lb.	.09	.09	.07
66° tks. wks.....ton	15.00	15.00	15.00
Oleum, 20%.....ton	19.00	19.00	18.00
Alum, Ammonia, lump.....lb.	.03½	.03½	.03½
Potash, lump.....lb.	*.03½	*.03½	*.03½
Chrome.....lb.	.05½	.05½	.05½
Soda, ground.....lb.	.04	.04	.04
Aluminum Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.09	.09	.09½
Chloride, white gran...lb.	.07½	.07½	.07½
Ammonia, anhydrous.....lb.	.30	.30	.30
Ammonia Water, drums, 26° lb.	.07½	.07½	.07½
Arsenic, white.....lb.	.12	.12½	.15½
Barium Chloride.....ton	*82.50	*82.50	*92.50
Nitrate.....lb.	*.07½	*.07½	*.07½
Barytes, white.....ton	33.50	33.50	33.50
Bleaching Powd., 35%, works ..... 100 lbs.	1.65	1.25	2.15
Borax, cryst., bbls.....lb.	.05½	.05½	.05½
Bromine, pure, wks.....lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y.....ton	24.50	24.50	24.50
Chlorine, liquid.....lb.	.05½	.05½	.05½
Copper Sulfate..... 100 lbs.	5.00	5.00	6.25
Iodine, resublimed.....lb.	4.55	4.55	4.50
Lead Acetate, white crystals .lb.	.14	.14	.13
Nitrate.....lb.	.22	.22	.22
Red..... 100 lbs.	11.40	11.40	10.60
White (Carb.).....lb.	.09½	.09½	.08½
Lime, live and hydrated, bbl. lb.	.01½	.01½	.01½
Oyster shell.....lb.	.03½	.03½	.03
Lime Acetate..... 100 lbs.	4.00	4.00	3.50
Magnesium Carbonate, tech. lb.	.08	.08	.08
Magnesite, calcined.....ton	55.00	55.00	55.00
Phosphorus, yellow.....lb.	.35	.35	.32
Red.....lb.	.75	.75	*.30
Plaster of Paris, tech .....bbl.	3.30	3.30	3.30
Potassium Bichromate.....lb.	.09½	.09½	.10
Bromide, imported.....lb.	.17	*.17	.14½
Carbonate, calc., 80-85%.lb.	*.06½	*.06½	*.05½
Chlorate, cryst.....lb.	*.07½	*.07½	*.05½
Hydroxide, 88-92%.....lb.	*.07½	*.07	*.08
Iodide, bulk, U. S. P....lb.	3.75	3.75	3.60
Nitrate.....lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.17½	*.17½	*.16
Prussiate, red.....lb.	*.60	*.60	*.90
Yellow.....lb.	*.30	*.29	*.38
Salt Cake, bulk.....ton	24.00	24.00	28.00
Silver Nitrate.....oz.	.44	.44	.44
Soda Ash, 58%, bags... 100 lbs.	*2.00	*2.00	*2.00
Caustic, 76%, N. Y. 100 lbs.	3.70	3.70	3.50

\* Resale or Imported (not an American maker's price).

	Oct. 1	Oct. 15	Jan. 1923
Sodium Acetate.....lb.	.05	.05	.07½
Bicarbonate..... 100 lbs.	2.25	2.25	2.00
Bichromate.....lb.	.07½	.07½	.07½
Bisulfite, powd.....lb.	.04½	.04½	.04
Chlorate.....lb.	.06½	.06½	.06½
Cyanide, 96-98%.....lb.	.23	.23	.23
Fluoride, tech.....lb.	.09	.09	.09½
Hyposulfite, bbls.. 100 lbs.	2.90	2.90	3.60
Nitrate, 95%..... 100 lbs.	2.45	2.45	2.57½
Nitrite.....lb.	.07½	.07½	.08½
Prussiate, yellow.....lb.	.14	.14	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40°.....100 lbs.	.80	.80	.80
Sulfide, 60%, fused.....lb.	.04½	.04½	.05
Strontium Nitrate.....lb.	*.10	*.10	*.08½
Sulfur, flowers.....100 lbs.	3.00	3.00	3.00
Crude, mines.....long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n...lb.	.12½	.12½	.10½
Oxide.....lb.	.47	.47	.43
Zinc Chloride, U. S. P...lb.	.25	.25	.20
Oxide, bbls.....lb.	.08½	.08½	.07½

ORGANIC CHEMICALS

Acetanilide, U. S. P., bbls...lb.	.32	.32	.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.38	3.38	3.17½
Glacial.....100 lbs.	12.78	12.78	12.05
Benzoic, U. S. P.....lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums.....lb.	.28	.26	.32
50- to 110-lb. tins...lb.	.30	.28	.34
Citric, crystals, kegs....lb.	*.50	*.50	*.48½
Oxalic, cryst., bbls., wks.lb.	.12	.12	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.....lb.	.35	.35	.45
Tannic, U. S. P., bbls...lb.	.83	.83	.70
Tartaric, cryst., U. S. P...lb.	*.32	*.32	*.32
Acetone, drums.....lb.	.25	.25	.21
Alcohol, denatured, complete. gal.	.46	.46	.45
Ethyl, 190 proof, bbls...gal.	4.75	4.75	4.70
Amyl Acetate.....gal.	4.50	4.50	2.50
Camphor, Jap, refined, cases .lb.	.87	.86	.88
Carbon Bisulfide, c/1.....lb.	.06	.06	.06
Tetrachloride.....lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums .lb.	.35	.35	.35
Creosote, U. S. P.....lb.	.40	.40	.40
Cresol, U. S. P.....lb.	.25	.25	.25
Dextrin, corn.....100 lbs.	3.64	4.09	3.09
Imported Potato.....lb.	.07½	.07½	.09
Ether, U. S. P., 100 lbs.....lb.	.13	.13	.13
Formaldehyde, bbls.....lb.	.12½	.12	.16
Glycerol, dynamite, drums...lb.	.16	.16	.16½
Methanol, pure, drums.....gal.	1.05	1.05	1.35
Methylene Blue, med.....lb.	2.25	2.25	2.25
Petrolatum, light amber.....lb.	.04½	.04½	.03½
Pyridine.....gal.	5.50	6.00	2.75
Starch, corn, pow'd....100 lbs.	3.44	3.69	2.47
Potato, Jap.....lb.	.06	.06	.06½
Sago.....lb.	.05	.05	.03½



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Oct. 1	Oct. 15	Jan. 1923
Beeswax, pure, white.....lb.	.38	.36	.36
Castor Oil, No. 3.....lb.	.13	.13	.13
Ceresin, yellow.....lb.	.08	.08	.08½
Corn Oil, crude, tanks, mills...lb.	.10½	.08¾	.09¾
Cottonseed Oil, crude, f. o. b. mill.....lb.	.10	.09	.09½
Linseed Oil, raw, lc/l.....gal.	.90	.95	.87
Menhaden Oil, crude, mills...gal.	.47½	.50	.53
Neat's-foot Oil, 20°.....lb.	.16¾	.16¾	.18½
Paraffin, 128-130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	5.95	5.85	6.25
Rosin Oil, first run.....gal.	.45	.45	.45
Shellac, T. N.....lb.	.62	.62	.80
Sperm Oil, bleached winter, 38°.....gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.13¾	.13¾	.12½
Tallow Oil, acidless.....lb.	.09½	.10¾	.11½
Turpentine, spirits of.....gal.	1.00	1.03	1.56

METALS

Aluminium, No. 1, ingots.....lb.	.25	.25	.23
Antimony, ordinary.....100 lbs.	6.75	6.75	6.75
Bismuth.....lb.	2.75	2.75	2.75
Copper, electrolytic.....lb.	.13¾	.12½	.14¾
Lake.....lb.	.13½	.13	.14¾
Lead, N. Y.....100 lbs.	6.65	6.60	7.80
Nickel, electrolytic.....lb.	.29	.29	.36
Platinum, refined, soft.....oz.	116.00	116.00	118.00
Quicksilver, flask......75 lbs. ea.	61.00	61.00	73.00
Silver, foreign.....oz.	.65¾	.63¾	.63
Tin.....lb.	.42½	.41½	.39
Tungsten Wolframite...per unit	8.50	8.50	7.50
Zinc, N. Y.....100 lbs.	6.65	6.65	8.25

FERTILIZER MATERIALS

Ammonium Sulfate, expt. 100 lbs.	3.45	3.45	3.90
Blood, dried, f. o. b. N. Y. ....unit	4.00	4.00	4.70
Bone, 3 and 50, ground, raw...ton	25.00	25.00	28.00
Calcium Cyanamide, unit of ammonia.....	2.25	2.25	2.25
Fish Scrap, dried, wks.....unit	4.00	4.00	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	3.25	3.00
Florida, 70%.....ton	3.55	3.55	3.55
Florida, 74-75%.....ton	4.50	4.50	4.50
Tennessee, 72%.....ton	5.50	5.50	5.25
Potassium Muriate, 80%.....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago.....unit	3.65 & .10	3.65 & .10	4.75 & .10

COAL-TAR CHEMICALS

Crudes

Anthracene, 80-85%.....lb.	.75	.75	.75
Benzene, pure, tanks.....gal.	.25	.24	.30
Naphthalene, flake.....lb.	.07	.07	.06½
Phenol, drums.....lb.	.28	.26	.32

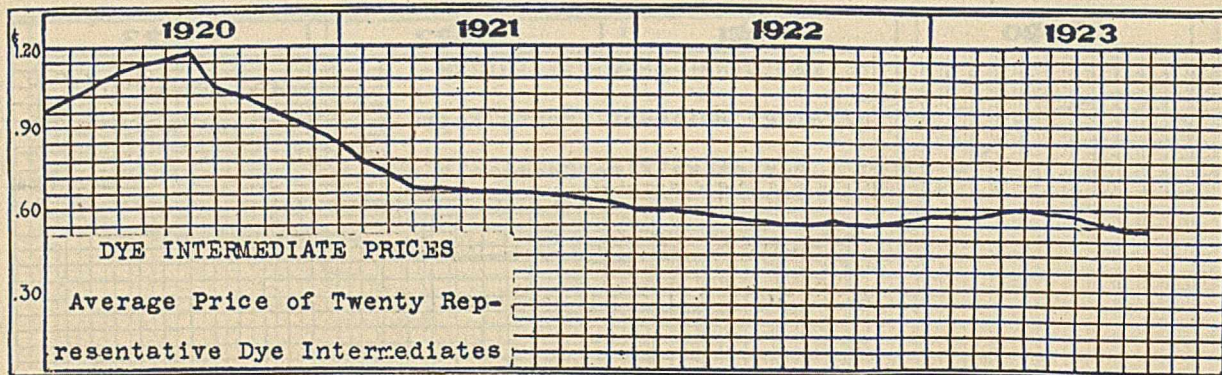
Crudes (concluded)

	Oct. 1	Oct. 15	Jan. 1923
Toluene, pure, tanks.....gal.	.27	.26	.30
Xylene, 2 deg. dist. range, drums.....gal.	.55	.50	—

Intermediates

Acids:

Anthranilic.....lb.	.96	.96	1.10
Benzoic, tech.....lb.	.70	.70	.65
Clevo's.....lb.	1.00	1.00	1.25
Gamma.....lb.	1.70	1.70	1.85
H.....lb.	.75	.75	.80
Metanilic.....lb.	.60	.60	.60
Monosulfonic F.....lb.	2.30	2.30	2.30
Naphthionic, crude.....lb.	.62	.62	.60
Nevile & Winther's.....lb.	1.10	1.10	1.15
Picric.....lb.	.25	.25	.20
Sulfanilic.....lb.	.20	.20	.19
Tobias'.....lb.	1.10	1.10	1.30
Aminoazobenzene.....lb.	1.15	1.15	1.15
Aniline Oil.....lb.	.16½	.16½	.17
Aniline Salt.....lb.	.24	.24	.25
Anthraquinone (sublimed)....lb.	1.30	1.30	1.30
Benzaldehyde, tech.....lb.	.75	.75	.65
U. S. P.....lb.	1.50	1.50	1.40
Benidine Base.....lb.	.82	.82	.84
Benidine Sulfate.....lb.	.70	.70	.70
Diaminophenol.....lb.	3.80	3.80	3.75
Dianisidine.....lb.	4.60	4.60	4.50
p-Dichlorobenzene.....lb.	.17	.17	.17
Diethylaniline.....lb.	.60	.60	.60
Dimethylaniline.....lb.	.41	.41	.41
Dinitrobenzene.....lb.	.19	.19	.19
Dinitrotoluene.....lb.	.19	.19	.20
Diphenylamine.....lb.	.48	.48	.50
G Salt.....lb.	.55	.55	.60
Hydroquinol.....lb.	1.25	1.25	1.05
Monochlorobenzene.....lb.	.10	.10	.10
Monoethylaniline.....lb.	1.00	1.00	1.00
b-Naphthol, dist.....lb.	.22	.22	.26
a-Naphthylamine.....lb.	.35	.35	.29
b-Naphthylamine.....lb.	.75	.75	.95
m-Nitroaniline.....lb.	.78	.78	.80
p-Nitroaniline.....lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol.....lb.	.75	.75	.72
o-Nitrotoluene.....lb.	.09	.09	.10
p-Nitrotoluene.....lb.	.50	.50	.65
m-Phenylenediamine.....lb.	.96	.96	1.00
p-Phenylenediamine.....lb.	1.45	1.45	1.50
Phthalic Anhydride.....lb.	.25	.25	.35
R Salt.....lb.	.55	.55	.55
Resorcinol, tech.....lb.	1.40	1.40	1.50
U. S. P.....lb.	2.25	2.25	2.00
Schaeffer's Salt.....lb.	.60	.60	.60
Sodium Naphthionate.....lb.	.62	.62	.62
Thiocarbanilide.....lb.	.35	.28	.35
Tolidine (base).....lb.	.95	.95	.95
Toluidine, mixed.....lb.	.31	.31	.30
o-Toluidine.....lb.	.18	.18	.15
p-Toluidine.....lb.	.90	.90	1.00
m-Toluylenediamine.....lb.	.90	.90	.95
Xylidine.....lb.	.50	.50	.42



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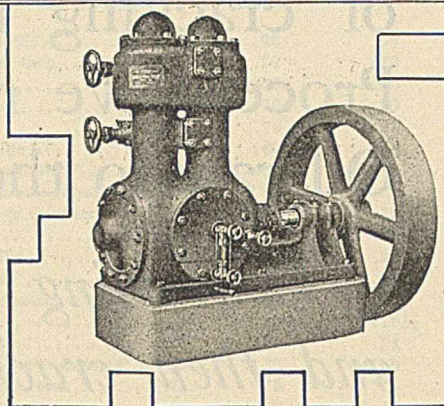
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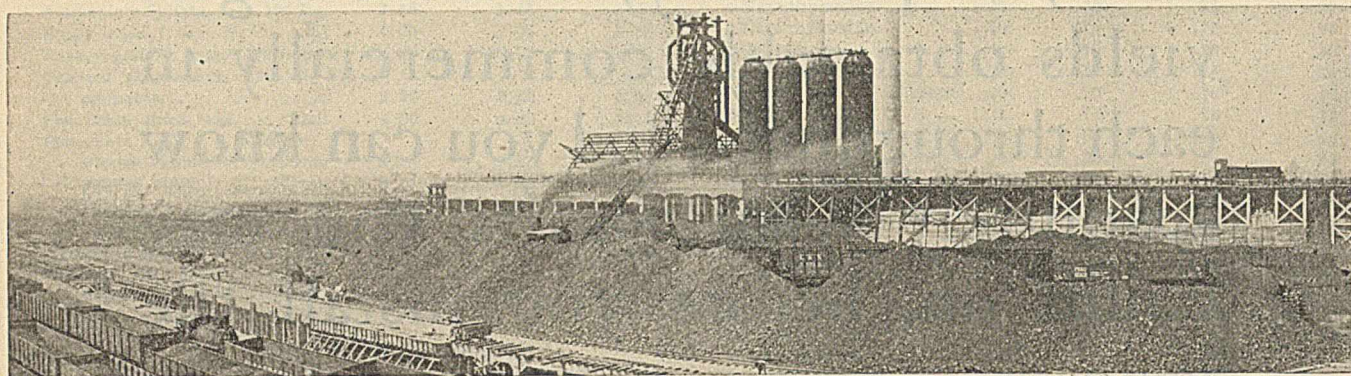
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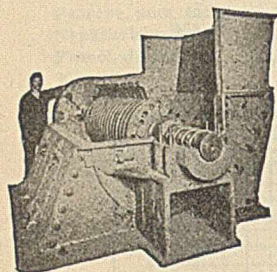
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# Eastman Organic Chemicals

Part of price List page showing Purity Data

T 1039	Primuline (Techn.).....
653	• Propionaldehyde BP 49-51°.....
675	• Propionamide MP 76-77°.....
799	• Propionanilide MP 103°.....
396	• Propionic Acid BP 139.5-141.5.....
T 396	Propionic Acid (Techn.) BP 130-140°.....
1291	• Propionic Anhydride BP 164-166°.....
P 528	• Propionitrile (Pract.) BP 96-97°.....
788	• Propionyl Chloride BP 78-82°.....
1235	• Propiophenone MP 16-18°, BP 105-107°/14 mm.....
747	• n-Propyl Acetate BP 99-102°.....
279	• Iso-Propyl Acetate BP 87-88°.....
848	n-Propyl Alcohol BP 96-98°.....
212	Iso-Propyl Alcohol (98-99%) BP 80-81.....
P 212	Iso-Propyl Alcohol (94-95%).....
1216	• n-Propylamine BP 48-50°.....
875	• Iso-Propylamine BP 33-35°.....
786	• n-Propylaniline BP 105-110°/15 mm.....
1481	• Iso-Propylbenzene see Cumene.....
990	Iso-Propyl Benzoate BP 94-96°/12 mm.....
609	• n-Propyl Bromide BP 70-71°.....
213	• Iso-Propyl Bromide BP 59-61°.....
1154	n-Propyl n-Butyrate BP 142-144.5°.....

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are given for most of our 1700 or more organic chemicals. These data, obtained from actual laboratory observations, may be regarded as specifications of quality below which our chemicals will not fall.

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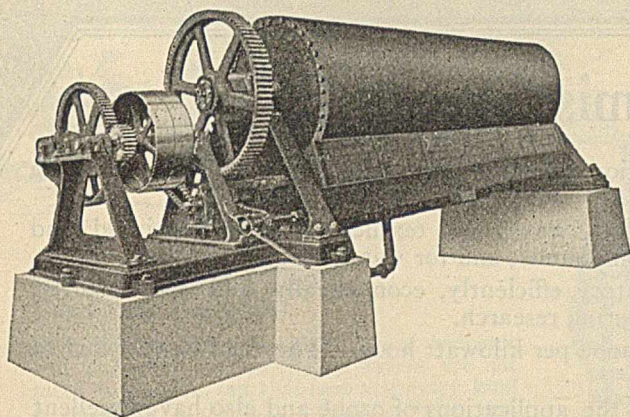
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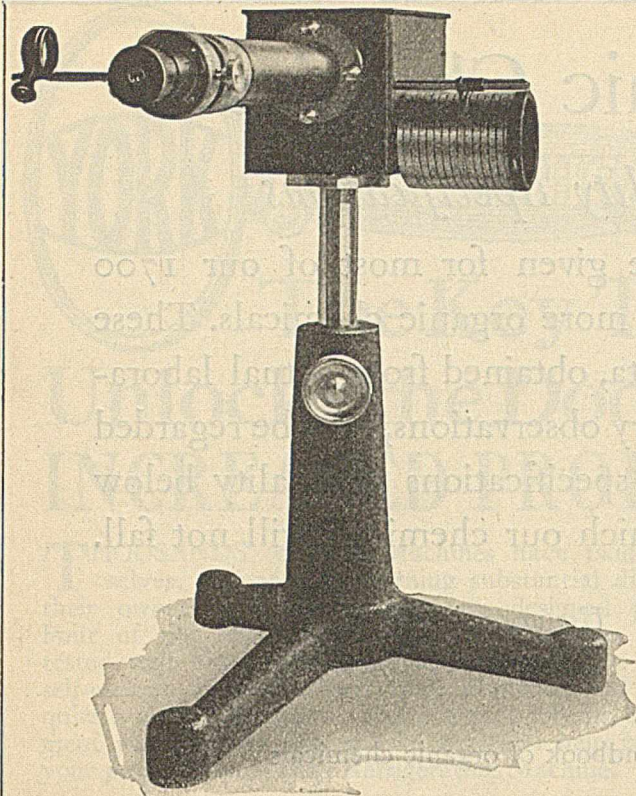
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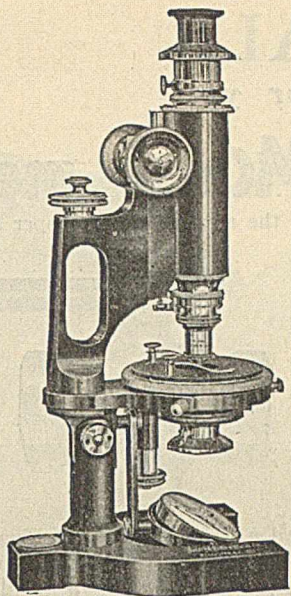
Their efficiency is approximately 50 grams of ozone per kilowatt hour. They can be supplied to furnish any required quantity.

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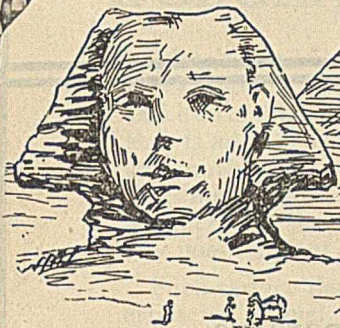
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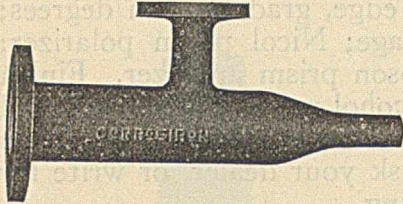
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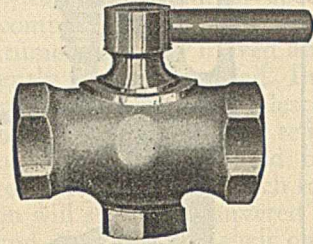
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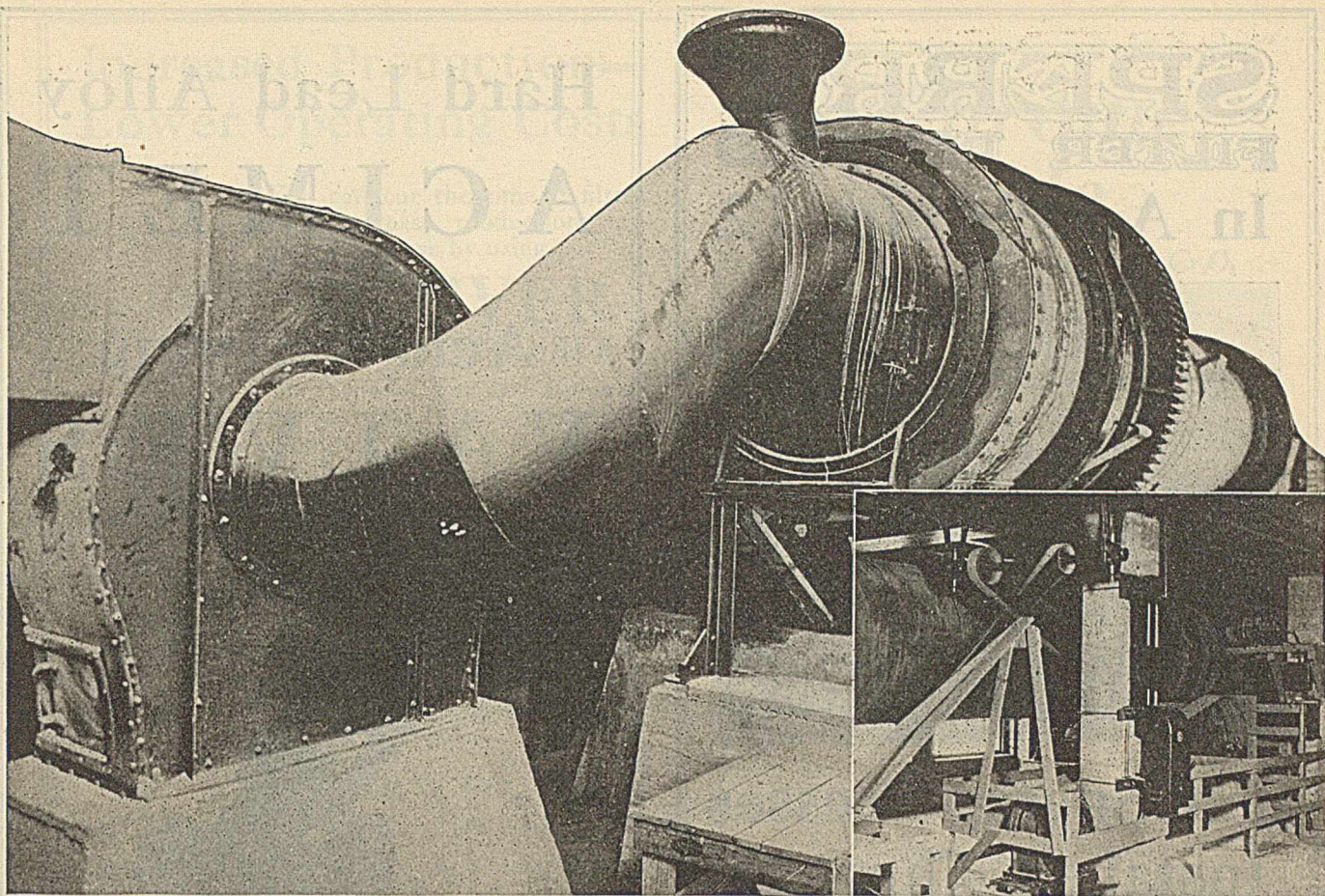
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*General view of dryer in operation; driving unit in foreground. This dryer is set up so that coal or electricity may be used as a heating element.*

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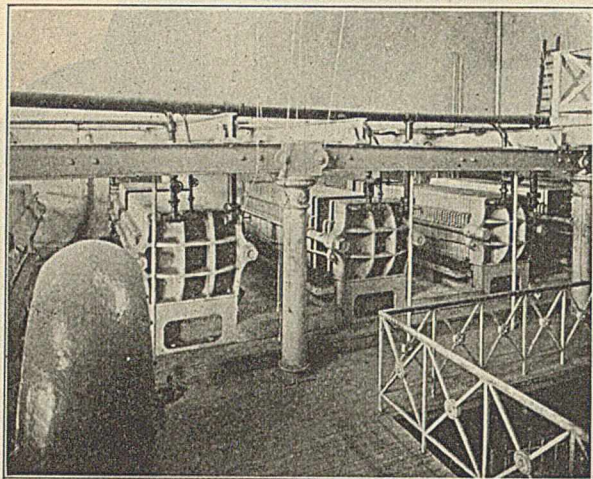


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In Action No. 12



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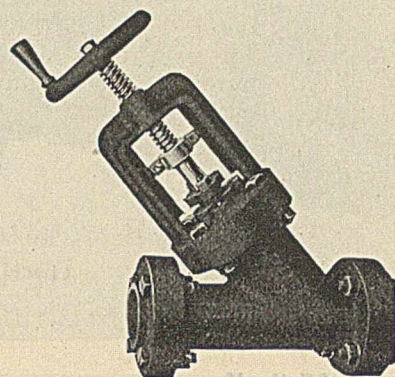
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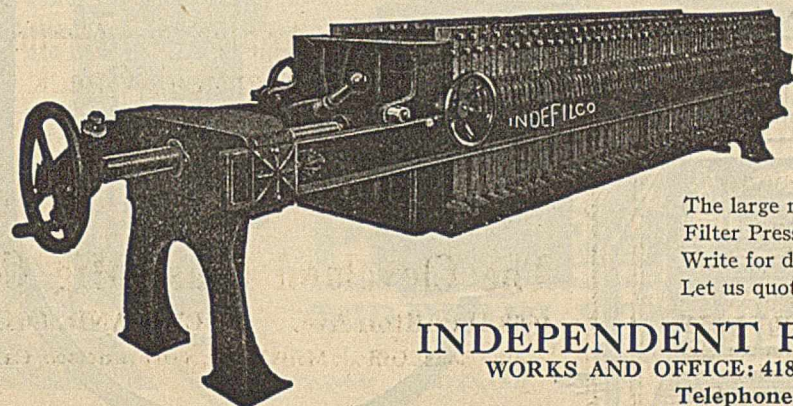
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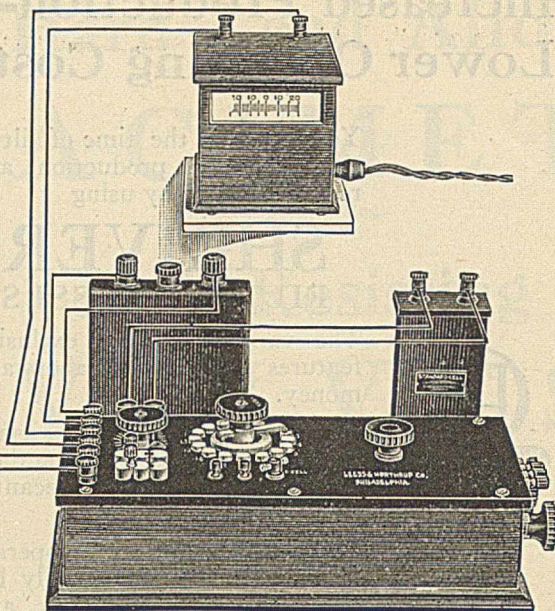
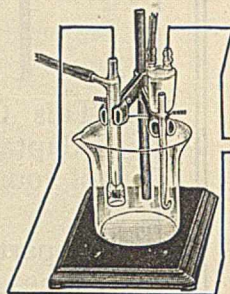
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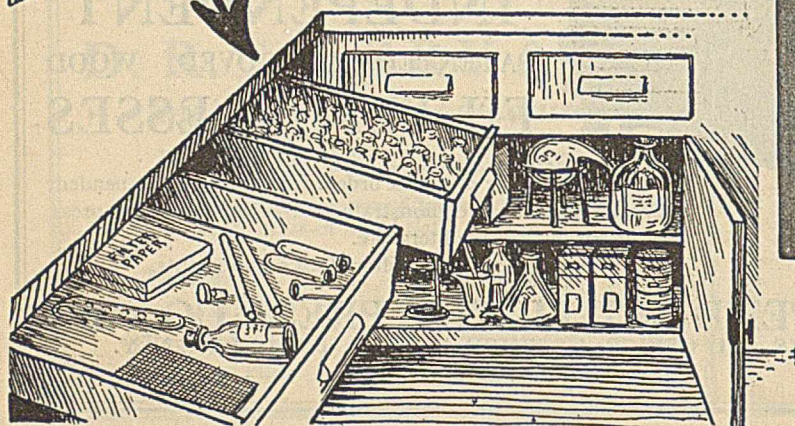
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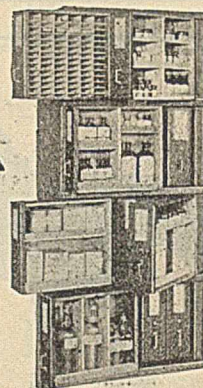
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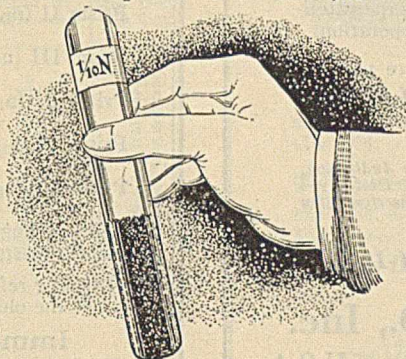
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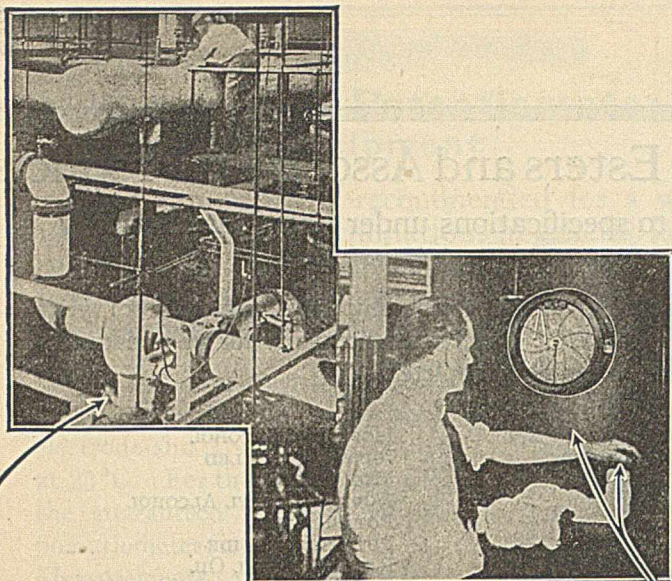
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## This hand tells the story

To regulate this brine cooler, they had to journey from the control valve (shown by the arrows) to a thermometer behind some pipes at the back of the cooler, then up a ladder at the far end of the room to the thermometer atop the cooler and from there back to the valve—and after setting the valve the only way to tell whether it was right was to make the trip again.

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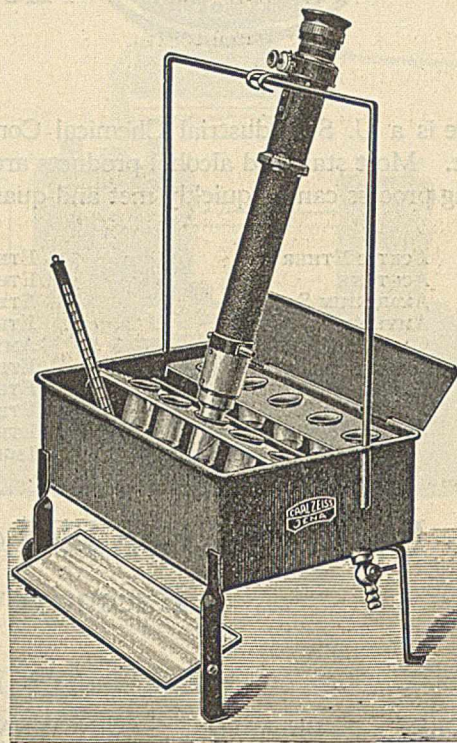
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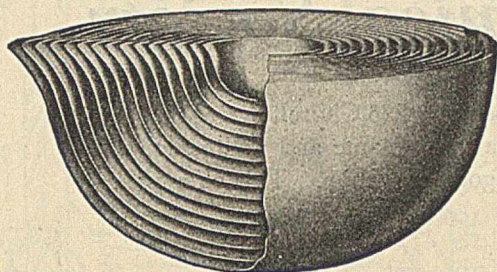


FIG. 6

## PLATINUM DISHES, WITH OR WITHOUT LIPS

Round Bottom—Hammered and Guaranteed

Capacity in C. C.	Approximate Weight in Grammes	Diameter Cm.	Depth Cm.
15	5	3.8	1.0
20	6	4.2	2.0
25	8	4.4	2.2
35	12	4.8	2.4
50	17	5.6	2.7
65	22	6.5	3.0
75	25	6.5	3.3
100	33	7.2	3.5
125	42	7.8	3.7
150	50	8.4	3.7
175	55	8.9	4.1
200	67	9.4	4.3
250	80	9.8	4.5
300	94	10.4	4.8
350	117	11.1	5.0
400	133	11.5	5.4

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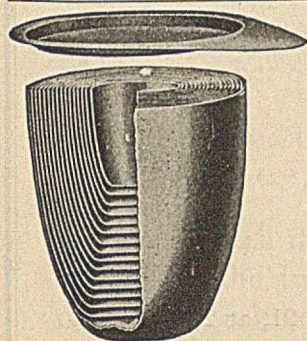


FIG. 4

8 C. C. to 110 C. C., Inclusive

Capacity in C. C.	Approximate Weight in Grammes	Diameter and Depth in Cm.
8	8	2.2
10	10	2.5
15	15	3.0
20	20	3.3
25	25	3.5
30	30	4.0
40	40	4.2
50	50	4.4
60	57	4.7
70	63	5.0
80	70	5.3
90	77	5.4
100	84	5.6
110	90	5.7

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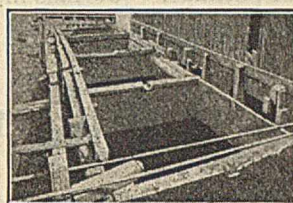
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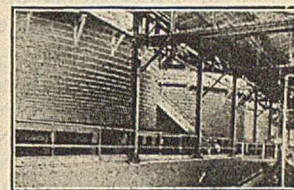
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# For tanks and Vats— REDWOOD

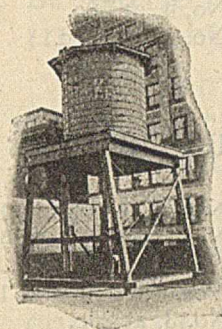
*A natural, odorless preservative which permeates Redwood during growth gives Redwood tanks and vats unusual resistance to moisture and chemical solutions. It protects Redwood against all forms of fungus decay and against insect activity.*



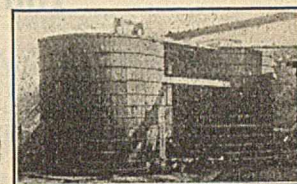
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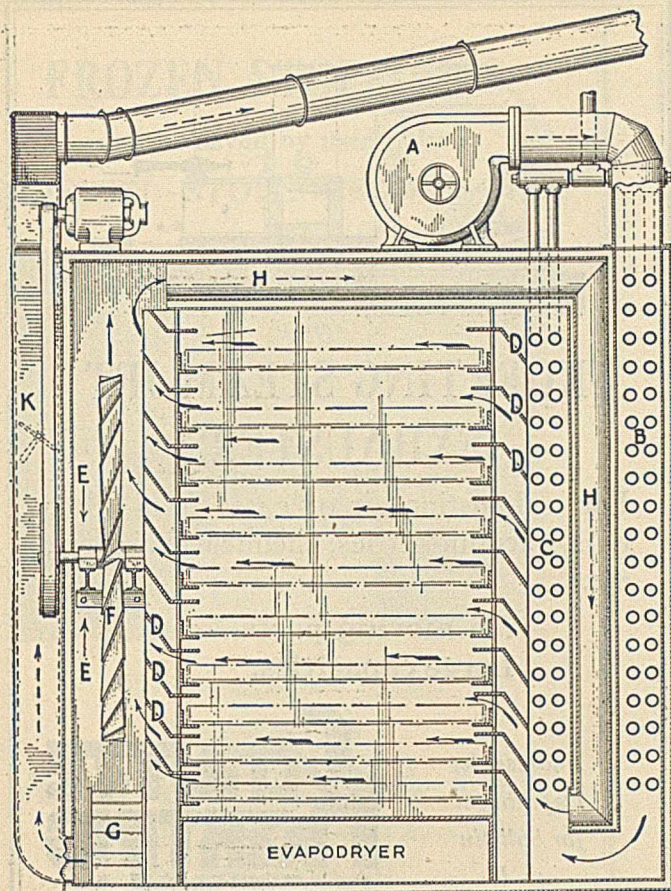
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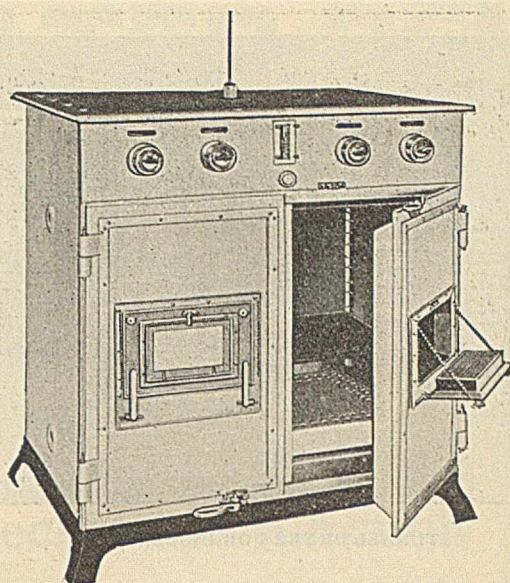
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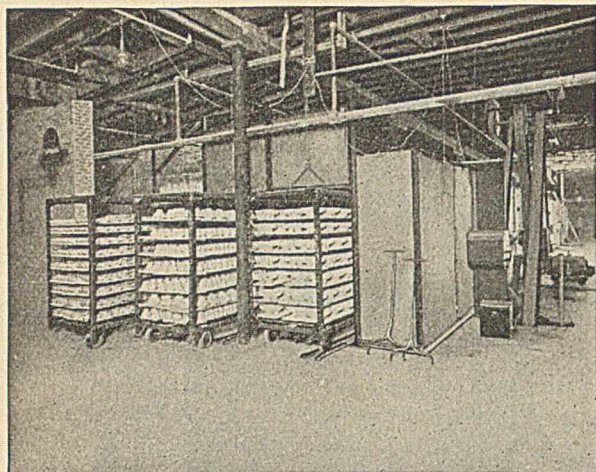
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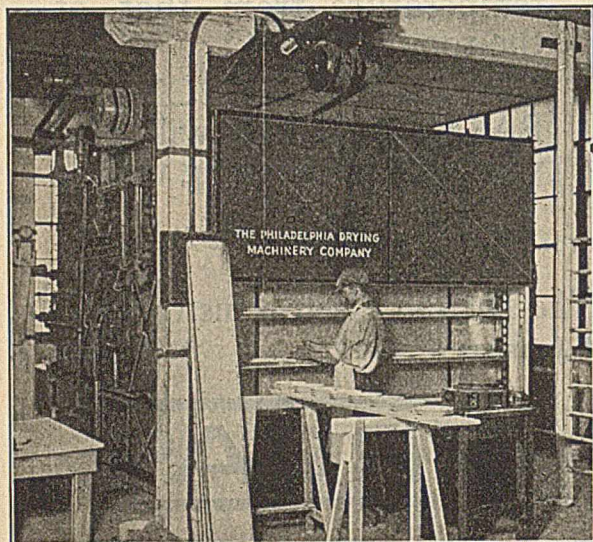
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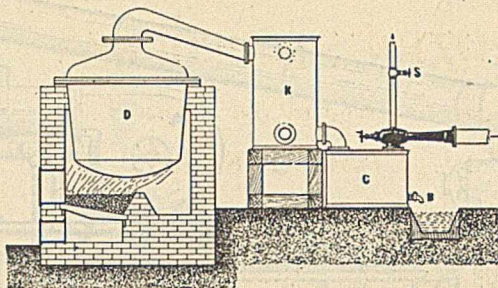
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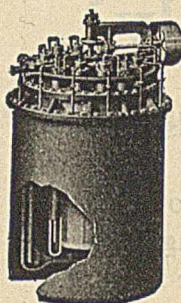
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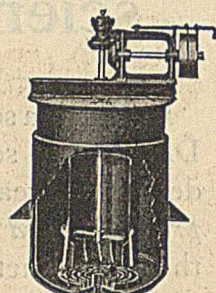
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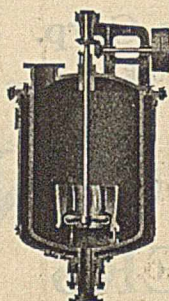
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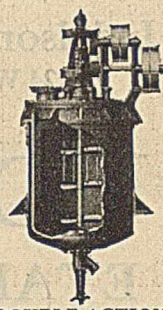


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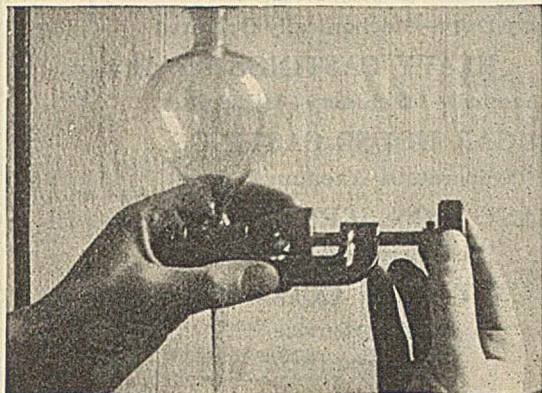
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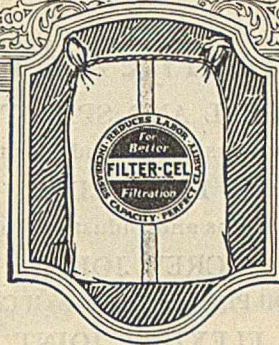
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# FILTER-CEL



## Mechanical in Action

**T**HE Filter-Cel process of commercial filtration is purely mechanical in action.

Filter-Cel is a microscopically porous, cellular mineral powder which is neither alkaline nor acid and has no chemical effect upon most liquors.

Perfect mechanical filtering action results because of the extremely fine porosity of the cake which Filter-Cel builds on the filter surface. The liquid is forced through these minute channels and as the most finely divided solids and gums are completely retained, only clear liquor passes through.

Filter-Cel not only gives increased clarity but because of the fact that a fresh filtering surface is constantly being deposited on the cloths, it greatly increases rate of flow and maintains this flow for longer cycles.

Complete information on the use of Filter-Cel in commercial filtration gladly sent upon request. Mail the coupon or write nearest office for Bulletin HH-40.

## CELITE PRODUCTS COMPANY

New York-11 Broadway Chicago-53 W. Jackson Blvd. San Francisco-Monadnock Bldg.  
Offices and Warehouses in Principal Cities  
CELITE PRODUCTS LIMITED, New Birks Bldg., Montreal, Canada

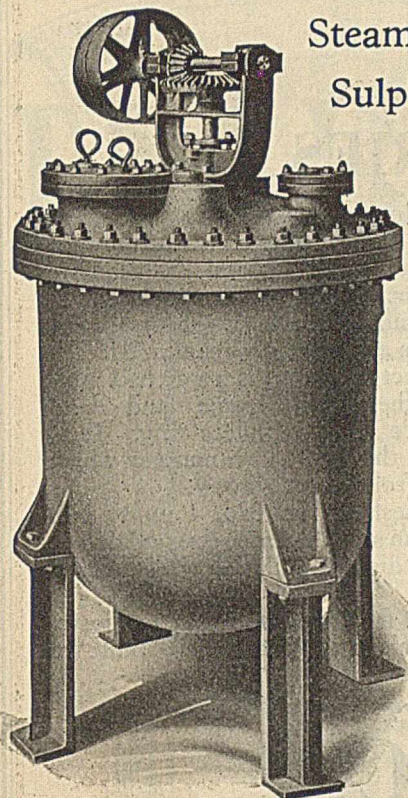
### Cellite Products Company

Without obligation send Bulletin HH-40 showing how Filter-Cel improves clarity, increases rate of flow and secures longer operating cycles.

Name .....  
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With Mixing  
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*Send  
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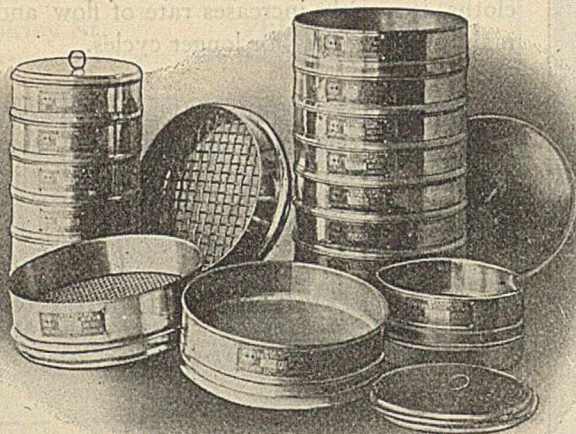
Chicago: 122 S. Michigan Blvd.  
St. Louis: Security Bldg.  
Birmingham: 1002 American Trust Bldg.  
Dallas: Magnolia Bldg.  
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Minneapolis: Plymouth Bldg.  
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Where absolute accuracy is required, together with substantial construction for constant service, Multi Metal Sieves are usually called for.

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If you do not trap your steam lines sufficiently, live steam can go straight to the sewer—and with it goes the cost of the coal burned to produce the steam. Just one untrapped ¾" steam pipe would waste more than a ton of coal every 52 hours.

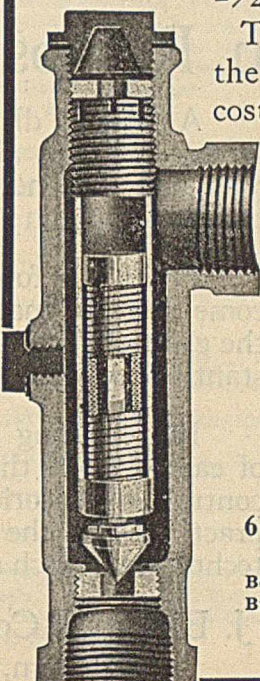
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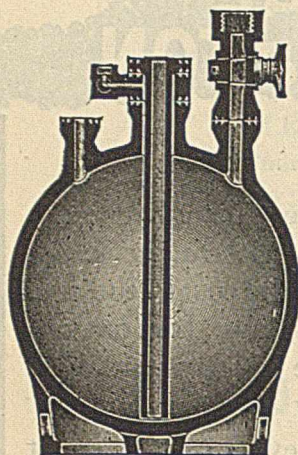
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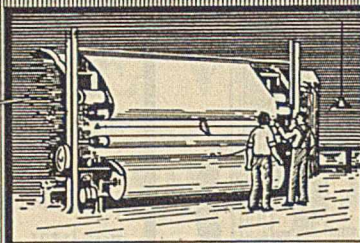
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B



## In Retrospect

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