

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume III

JULY, 1911

No. 7

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Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

EDITORIALS

RETROSPECTION.

We may not need special evidence to convince ourselves that we are living in a rapidly improving technical age. The development of our industries testifies clearly on this point. That chemistry has an important part in this development, particularly in our own country, could be guessed from a knowledge of the fact that there are fully ten times as many chemists here as there were twenty years ago. These men are at work on more than ten times as many different materials as were known twenty years ago, and the end is not yet.

An interesting and instructive view of the rate of advance of chemistry in our era may be gained from a study of the known metallic elements.

It is plain that new chemical compounds, in general, are coming into commercial use so rapidly that it is hopeless to even attempt collection of data. It is safe to say that if we include organic compounds, there are many hundreds of new substances made and described each year. Hundreds of these will be useful for years, solely as systematizing marks for themselves and for other compounds, but in this way a very strong foundation is being built for the future of chemistry. Any adequate summary for this general field is impracticable because of its magnitude.

In case of the chemical elements a survey is more simple, and particularly with the metallic elements. The metallic elements have a special interest in this connection, because they are limited in number, their properties are known and some of them have been used for ages. A philosopher would probably maintain that as our wants become more and more differentiated, we will call into use more and more of this store of metals. This is practically what has been done in the past. That we still have no considerable use for metallic barium, for example, is explained by

an insufficiently developed requirement. More easily obtainable metals have thus far fulfilled needs which will finally grow so complex as to require metallic barium.

But this rate of increase in demand for new metals to fill new wants has not been a constant one—far from it. It never was nearly so rapid as at present, and it characterizes our technical age. We have in all about fifty elementary substances which we can call metals or metalloids. Not more than a very few others seem probable of discovery. We want to point out the rate of increase of use, to what we may call an appreciable extent, of these metals in their metallic state. This excludes from consideration uses of compounds or salts of the metals.

Of the fifty there were seven which were known and used commercially over two thousand years ago. These are iron, copper, tin, gold, silver, mercury, and lead. There are eight others which were introduced into practical use more or less extensively between the first and the nineteenth century. They are zinc, iridium, platinum, cobalt, nickel, antimony, cadmium, and bismuth, that is, the rate of addition has been less than one metal for each two centuries prior to our century. Within our own times, say about a quarter century, there have been about fourteen more metals added to commercial use, or a rate more than one hundred-fold greater than the previous rate.

These values may be modified somewhat by use of different criteria of commercial use, but the conclusions remain about the same.

We are now rapidly seeing practical use made of a large part of our little group of known metals. Those which have been introduced into commercial use during the past quarter century, either pure or intentionally alloyed, are aluminum, magnesium, silicon, cerium, vanadium, tungsten, tantalum, osmium, chromium,

selenium, molybdenum, titanium, boron and manganese. The rate of addition must soon rapidly fall off, but among those which seem to call for some attention and demand introduction is calcium. Its common occurrence promises a long and useful life, but thus far, its peculiar properties have not suited specific requirements. It will be interesting to watch its development. Can it possibly go through any such varied and complex series as iron has experienced, for example? At one time there was only a single kind of iron. It met the needs of the time. Later, we find the uses distributed over what was called cast iron, wrought iron, and steel. Then several entirely different cast irons and wrought irons appeared, each of which filled some particular use. Among the steels there are already a myriad of varieties. The carbon steels, which, for a long period of time, were the only steels, are now overshadowed by the special alloy steels, and it seems as though there would be no end to this development. Nickel steels find use in armor plate. Tungsten and chromium steel is the leader in high-speed cutting tools. Molybdenum steel makes most useful permanent magnets for electric meters. Silicon steel fits best the demands of electric transformers, because of its low magnetic hysteresis and high resistivity. Titanium steel is said to be superior for railroad rails. Vanadium steel is apparently particularly valuable for springs, and thus the list grows. All of these alloy steels are the product of the last quarter century, and it is perfectly evident that with the introduction of electric furnaces, the special steel alloys are bound to be still further developed.

W. R. WHITNEY.

HEAT TRANSFER.

In view of the fact that heat transfer apparatus, including all forms of boilers, evaporators, condensers, liquid and gas heaters and coolers, represent so much greater engineering and industrial investment yearly than heat-transforming apparatus like the steam engine and gas engine proper, that there is so little information on the laws of heat transfer, fundamental to the design of the former while numberless books are full of discussions of the laws of transformation supposedly fundamental to the design of the latter, great sums of money are yearly spent in improvement of engines, but very little has been done to increase the capacity of heat transfer surfaces to reduce the size of evaporators, condensers, heaters and coolers. That possibilities of great improvement exist is apparent from the following review. It seems almost axiomatic to say that the rate of heat flow from a region of high temperature to one of low is directly proportional to the difference between those temperatures, and, therefore, that a coefficient generally designated as U will represent the B. t. u.'s transmitted per square foot per degree per hour should have a constant value. How strange it is then to find that the value of U when derived from experimental or engineering practice is found to vary from less than 2 to nearly 1000, with no adequate explanation. The values of $U = 1.8$ are

found in refrigerating rooms with still air when either ammonia or brine is in the pipes, and this value is increased to perhaps 5 or 6 by a vigorous circulation with air velocities up to 900 feet per minute. On the average, however, for these refrigerating pipes, absorbing heat from and giving it to either liquid brine or evaporating ammonia, the value $U = 2.5$ will be found representative. This is very close to the common value of $U = 2$ for steam radiators where heat is passing from condensing steam to mildly circulating air, and likewise, close to the values for steam pipe condensation which lie between $U = 2.5$ and $U = 4.0$, depending on quite a variety of conditions, such as material, color, surface conditions, steam pressure and air circulation. When the heat passes from products of combustion to steam in steam superheaters, the average value is about $U = 4$. Economizers have values lying between $U = 2$ and $U = 3.5$, depending on circumstances and about the same order of magnitude is found in steam boilers which, however, are somewhat different on account of direct radiation influences.

In tank brine coolers where the evaporating ammonia absorbs heat from sluggishly circulating brine in the tank covering the pipe coils, the value $U = 10$ is about right when the vapor leaves the coil reasonably dry. This, however, rises to about $U = 14$ when the coil is flooded with ammonia, compelling the vapor bubbles to pass through liquid to the end of the coil. With double pipe brine coolers, evaporating ammonia absorbing heat from circulating brine, the coefficient is higher and will lie between $U = 30$ and $U = 50$ for velocities between 100 and 200 ft. per minute. A similar range is found in liquid heat exchangers of absorption refrigerating systems, the value being between $U = 50$ and $U = 60$, depending on the velocity, the latter figure corresponding to a velocity of 650 feet per minute. This value of $U = 60$ is common to other apparatus involving the passage of heat from liquid to liquid or liquid to evaporating liquid. It applies directly to water and beer coolers, the liquid trickling over pipes with ammonia evaporating inside. When, however, the heat transfer is from liquid outside to circulating brine inside, it rises to $U = 75$. The absorbers of ammonia vapor where the ammonia is cooled by water inside, the value is again $U = 60$. The same value applies to open-air ammonia condensers with heat flow from condensing ammonia to water trickling over the outside of the coils. Shell type brine coolers and condensers in which brine or water is circulated through coils, and ammonia evaporated or condensed between coil and shell have a coefficient about $U = 100$. Steam surface condensers similarly constructed have values between $U = 130$ and $U = 200$, depending somewhat on the water velocity, freedom from air and ratio of circulating water to steam. A commonly used value is $U = 180$, reported long ago by Loring and Emery. This same value is used in and found to apply well to some forms of feed-water heaters in which the transfer is of the same class as the sur-

face condenser, *i. e.*, heat flow from condensing steam to circulating water, but recent tests of feed-water heaters show the same peculiarity as was mentioned in the case of double pipe brine coolers—a rise of the coefficient with water speed to values close to $U = 1000$, although few designers would think of exceeding $U = 350$ for these heaters. Passage of heat from condensing liquid to boiling liquid at lower temperature is a characteristic of evaporators of single and multiple effect, and for these $U = 300$ is a fair average value. It is interesting to note that this same value also applies to the generators of absorption refrigerating machines where the heat of condensing steam is given up to rich aqua ammonia liquor.

There is probably no single class more interested, consciously or unconsciously, in increasing the effectiveness of heat transfer surfaces than chemical manu-

facturers, and there is likewise no class with the opportunities for securing the great mass of data necessary for the formulation of laws of design with equal ease. There is presented in this issue a paper on the subject, discussing the various physical constants involved, which, while it leaves much to be said on the subject, will serve to open a thorough investigation of it in these pages. It is hoped that all the users of heat transfer apparatus will send in letters and criticisms of this paper, possibly preparing additional papers, but more important than all else, large quantities of data on every form of heat transfer apparatus in their establishments, all of which we will undertake to print as part of a campaign of improvements that is needed at least as much, if not more, than any other single thing common to all interests.

C. E. LUCKE.

ORIGINAL PAPERS.

HEAT TRANSMISSION.

By HAROLD P. GURNEY.

Received March 22, 1911.

It is the purpose of this paper to evolve and present a rational method of analyzing problems in heat transmission along the lines laid down by such eminent and practical authorities as Hausbrand,¹ Mollier,² and Berlowitz.³ The study of the flow or transmission of heat has important bearings in mechanical, electrical, and chemical engineering, and it is a subject which merits a more systematic treatment than is usually accorded to it.

The usual technical case of heat transmission is where heat flows from a relatively hot fluid through a separating plate to a cold fluid. The fluids are usually air, hot gases, water, or steam; in chemical work, the number is almost without limit. The plate is usually thin and of metal, and may be flat, spherical, or tubular in shape. Either or both fluids may be moved parallel or perpendicular to or against the plate, or portions of the plate.

In heat flow, the temperature gradient may be defined as the rate of change in temperature with respect to distance in the direction that the heat is moving; in ordinary units, it is the drop in Fahrenheit degrees per linear inch in the direction of heat flow. When heat is moving uniformly from fluid to fluid through a plate, the temperature gradient is constant throughout the plate. Here the temperature gradient is determined by the rate of heat flow which is constant, and the heat conductivity (or resistivity) of the plate material. In the fluid, the temperature gradient is not constant, it is a maximum at the boundary surface and drops off as the distance from the boundary or plate surface increases. In an infinitesimal film just next to the plate, the temperature gradient is determined solely by the rate of heat flow and by

the true conductivity of the fluid. Beyond this, heat flow results not only from true conductivity, but also from actual transportation of portions of the fluid in the direction of heat flow. This is called convection and it is the heat-transporting power of the fluid. The convectivity of a fluid at any point depends on: (1) the increase in density of the fluid per unit change of temperature, (2) the density, (3) the viscosity, (4) the mean distance from the fluid boundary, and (5) the velocity. It may further be observed that in the plate, the heat flow is constant, whereas in the fluid, the heat flow is greatest at the surface of the plate and diminishes to nothing at a point or points farthest from the plate.

From a practical point of view, it is usual to consider an abrupt drop in temperature from the plate surface to the fluid to exist, and to assume that the fluid has the same temperature throughout. This temperature is the mean effective temperature of the fluid, and, by definition, it is the temperature it would attain if completely mixed without gain or loss of heat. This is a temperature which is different for different parts of an apparatus, and while practically its initial and final values may be readily measured, its intermediate values are obtained with difficulty. For example, the temperature of water circulating through heating coils can be measured before it goes in and after it comes out, but the mean effective temperature at any cross section of the coils is not so easily determined.

Diagrammatically, this discussion may be made clearer by the two following distance-temperature plots. Actually the temperature follows the curve shown in A, but for convenience of treatment, it is assumed to follow the broken curve in B.

This differentiates heat conductivity into two distinct forms: (1) solid heat conductivity where heat traverses a solid or a fluid at rest; and (2) surface heat conductivity where heat passes between a solid and a fluid. The first is the internal conductivity,

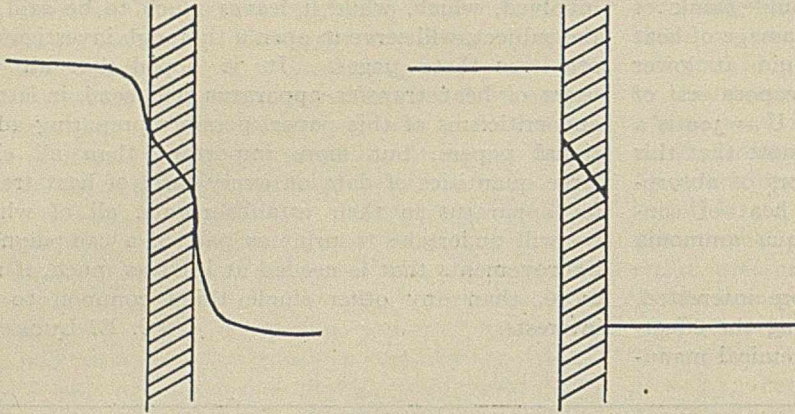
¹ Verdampfen, Kondensieren, and Kühlen, 1909.

² Zeitschrift des Vereines deutsche Ingenieure, 1897.

³ Zeitschrift für Apparatenkunde, 1908.

and the second is the boundary conductivity or external conductivity when referred to a plate separating two fluids. The first form of conductivity is a physical characteristic or property of matter. The second form depends not at all on the solid from

The external resistance is the resultant and preceding sum of the boundary resistances of the two sides of the plate. The resistance of a square foot on one side is ζ_1 and on the other side is ζ_{11} ; separate resistances of both sides are ζ_1/A and ζ_{11}/A , and



$$Z_o = \frac{\zeta_1}{A} + \frac{\zeta_{11}}{A}$$

The external resistance of a square foot is z_o

$$z_o = Z_o A = \zeta_1 + \zeta_{11}$$

and

$$Z = \frac{\zeta_1}{A} + \frac{\rho\delta}{A} + \frac{\zeta_{11}}{A}$$

The resistance of a square foot of plate both internal and external is z . Then,

$$z = ZA = \zeta_1 + \rho\delta + \zeta_{11}$$

and

$$Q = \frac{\Delta AT}{\zeta_1 + \rho\delta + \zeta_{11}}$$

These same facts may be expressed in terms of conductances and conductivities instead of resistances

which heat is passing, but on the fluid and especially on such factors as (1) the conductivity, (2) the density and viscosity, (3) the expansiveness to heat, (4) the mean hydraulic radius of the space occupied by the fluid, and (5) the mean fluid viscosity.

In order to investigate quantitatively the flow of heat, a system of notation is here used which is consistently adhered to. Q is the heat units in British thermal units which flow through a heat-transmitting plate in a time T hours, where the temperature difference between the two fluids on either side is Δ degrees Fahrenheit. Z is the heat resistance of the plate. A strict proportionality between the rate of heat flow and the drop in temperature may be assumed. The ratio of the temperature drop to the rate of heat flow may be defined as the resistance, the reciprocal of conductance.

$$Z = \frac{\Delta}{Q}, \quad Q = \frac{\Delta T}{Z}$$

The resistance Z is made up of two separate component resistances: (1) the internal resistance Z_1 of the plate, and (2) the external resistance Z_o , the sum and resultant of the boundary resistance of the plate.

$$Z = Z_1 + Z_o$$

The resistance possessed by a portion of the plate of one square foot area and one inch in thickness is the specific internal resistance or the internal resistivity and is designated by ρ . The area of the plate is A square feet, the thickness is δ inches, and the internal resistance is Z_1 . The plate resistance is proportional to its thickness and to the inverse of its area.

$$Z_1 = \frac{\rho\delta}{A}$$

The internal resistance of a square foot of plate of thickness δ inches is z_1 .

$$z_1 = Z_1 A = \rho\delta$$

and resistivities, but it must be observed that where resistances in series are additive, conductances in series are not additive. The resultant of conductances in series is the reciprocal of the sum of the reciprocals of the separate conductances. This results from the fact that conductance is the reciprocal of resistance and is the ratio of heat flow to the temperature drop. If G be used to designate conductance, then,

$$G = \frac{Q}{\Delta} = \frac{\text{rate of heat flow}}{\text{temperature drop}}$$

hence,

$$Q = \Delta TG$$

The conductance G is the resultant of the internal conductance G_1 and the external conductance G_o ,

$$G = \frac{1}{\frac{1}{G_1} + \frac{1}{G_o}}$$

The specific internal conductance or the internal conductivity is the conductance of a portion of plate of one square foot area and one inch thickness and is designated by λ the reciprocal of ρ . Since the internal conductance is proportional to the area of the plate and inversely as its thickness, then,

$$G_1 = \frac{A\lambda}{\delta}$$

The internal conductance per square foot is g_1 .

$$g_1 = \frac{G_1}{A} = \frac{\lambda}{\delta}$$

The boundary conductances per square foot, or the boundary conductivities are $r_1 = 1/\zeta_1$ and $r_{11} = 1/\zeta_{11}$ and G_o is the external conductance.

$$G_o = \frac{A}{\frac{1}{r_1} + \frac{1}{r_{11}}}$$

The external conductance of a square foot is g_o .

$$g_0 = \frac{G_0}{A} = \frac{1}{\frac{1}{r_1} + \frac{1}{r_{11}}}$$

Then the combined conductance G of the plate, both with respect to internal and external conductances is given by the following expression:

$$G = \frac{A}{\frac{1}{r_1} + \frac{\delta}{r} + \frac{1}{r_{11}}}$$

The conductance per square foot is G ,

$$g = \frac{G}{A} = \frac{1}{\frac{1}{r_1} + \frac{\delta}{r} + \frac{1}{r_{11}}}$$

and

$$Q = \frac{\Delta AT}{\frac{1}{r_1} + \frac{\delta}{\lambda} + \frac{1}{r_{11}}}$$

In most heat-transmitting apparatus, the temperature drop is not the same at all points of the drop. The equations deduced hold for infinitesimal plate areas, but by adopting a mean temperature drop in the place of Δ , they may be applied to finite areas. The maximum and minimum temperature differences may always be obtained from measurements on the temperatures of both fluids both before and after transit through the apparatus. The simplest mean temperature difference would be either the arithmetic average, or the geometric mean of the maximum and minimum, but the former is too high, while the latter is too low. The most rational mean is the logarithmic mean and it is obtained by considering the temperature difference to vary relative to time, or distance traversed at a rate proportionate to its instantaneous value. If Δ_0 is the minimum temperature difference, Δ_1 the maximum temperature difference and Δ_m the mean temperature difference, then the latter may be expressed in terms of the two former by the following expression:

$$\Delta_m = \frac{\Delta_1 - \Delta_0}{\ln \Delta_1 - \ln \Delta_0}$$

Let the ratio of Δ_0 to Δ_1 be a variable, x .

$$\Delta_m = \Delta_1 \frac{1-x}{-\ln x}$$

An arithmetic mean would be $\Delta_1 \frac{x+1}{2}$, while a geometric mean would be $\Delta_1 \sqrt{x}$. The following table brings out the relations between the three means.

x	$\frac{x+1}{2}$	$\frac{x-1}{\ln x}$	\sqrt{x}
1.000	1.000	1.000	1.000
0.900	0.950	0.949	0.949
0.800	0.900	0.896	0.895
0.700	0.850	0.841	0.836
0.600	0.800	0.783	0.775
0.500	0.750	0.722	0.707
0.400	0.700	0.636	0.632
0.300	0.650	0.583	0.548
0.200	0.600	0.497	0.447
0.100	0.550	0.382	0.316
0.050	0.525	0.317	0.223
0.020	0.510	0.251	0.141
0.010	0.505	0.215	0.100
0.000	0.500	0.000	0.000

For design, the use of the geometric mean gives safer values than the logarithmic mean; for investigation, the logarithmic mean should be used. Occasionally, the arithmetic mean may be used.

Where both sides of a plate have the same area as in the case of a flat plate, no doubt arises as to the proper value of A ; but where the areas of both sides of a plate differ as in a pipe, the problem of obtaining a mean area presents itself for investigation. Since the mean heat-transmitting area is nearer in value to the area of the side where there is the greatest heat resistivity, a single mean area may be obtained by weighting the areas with the respective resistivities. The area A_1 has a heat resistivity, ζ_1 ; A_{11} has a heat resistivity, ζ_{11} , and A_m is the mean area.

$$A_m = \frac{\zeta_1 A_1 + \zeta_{11} A_{11}}{\zeta_1 + \zeta_{11}}$$

For a pipe A_0 and A_2 being the internal and external areas, Mollier gives the following formula:

$$A_m = \frac{\zeta_1 + \zeta_{11} + \delta \rho}{\frac{\zeta_1}{A_1} + \frac{\zeta_{11}}{A_{11}} + \frac{\rho \ln \frac{A_2}{A_0}}{2}} = \frac{\zeta_1 + \zeta_{11}}{\frac{\zeta_1}{A_1} + \frac{\zeta_{11}}{A_{11}}} \text{ approximately.}$$

A rough rule is to employ as mean area the area whose resistivity is greatest, except where the areas have about equal resistivities, and then an average is quite close.

Apparatus for transmitting heat between fluids may be classified under four types: (1) counter-current, (2) parallel current, (3) perpendicular current, and (4) single current. In counter-current apparatus, the fluids move in opposite directions, and the temperature difference does not generally vary greatly. In parallel current apparatus, the fluids move in the same direction; the temperature difference is at first large and rapidly diminishing, later it is small and slowly diminishing. In perpendicular current apparatus, the fluids move in directions at right angles to each other, and in this respect stands midway between counter-current and parallel current apparatus. In practice, perpendicular current and counter-current apparatus are sometimes placed in series and so become essentially parallel current or counter-current in effect. In single current apparatus, one fluid, and usually the fluid whose temperature it is desired to modify, remains in the apparatus during the entire operation while the heating or cooling fluid moves through at a constant rate. The use of the single current apparatus makes the process intermittent; with other types, the process is continuous.

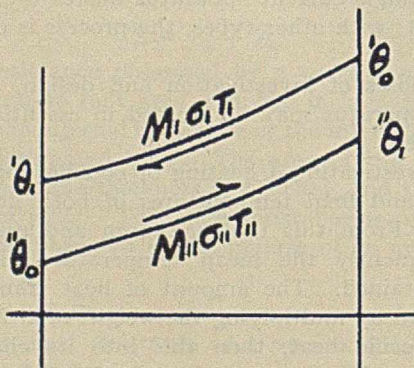
For purposes of investigation and design, all four types of apparatus may be treated in essentially the same manner.

When investigating a heating or cooling apparatus, the initial and final temperatures of both fluids are measured. From this the maximum and minimum, and consequently the mean temperature difference may be obtained. The amount of heat transmitted can be found by multiplying the weight of either fluid into its specific heat, then this into its change in temperature. If necessary, the heat lost in radiation

from the exterior of the apparatus may be taken into account. Knowing the area of the heat-transmitting plate or tubes, all data necessary to compute the heat-transmitting capacity of the walls is at hand.

When designing an apparatus, the heat-transmitting capacity of the plates must be previously estimated from data available or assumed. A preliminary assumption on this point to determine within certain limits the velocities of the fluids, and from this a closer final assumption may be made. The rate at which heat is to be transmitted is obtainable from the weight, specific heat, initial and final temperatures of the fluid whose temperature is to be raised or lowered, and the length of time assigned to the operation. With respect to the fluid supplying heat or cold, its initial temperature and specific heat may be regarded as fixed, but the amount delivered per hour and final temperature are interdependent variables. The most logical starting point in design is to make x a variable ratio of the variable temperature difference to the fixed temperature difference. For any value of x the rate of supply of heating or cooling fluid and the required surface, hence approximate size of apparatus, is easily computed. As x increases, that is, as a larger temperature difference and a smaller temperature change is obtained, the fluid supply rate becomes greater but the size of the apparatus becomes smaller. Against x as abscissae may then be plotted as ordinates the total amount of depreciation, interest, maintenance, and rental on apparatus plus the cost of fluid together with the pumping and storing of the same. The curve obtained will have a minimum, and the best value of x to adopt should be as near to this minimum as possible, at the same time taking into consideration other points of plant economy that would tend to shift this value. In the design of single current and perpendicular current apparatus, two variables similar to x may be chosen instead of one; a simple expedient in these cases is to employ, as abscissae, the products of the two variables and then later try the effect of shifting the ratio of these variables.

Owing to the variety of factors which may come into play, it is not advisable to lay hard and fast rules for the solution of problems in the design of heat-transmitting apparatus. A perfectly general mathematical method might not be at once soundly



theoretical or practical, but a brief outline of the simple mathematical aspects ought to be presented.

Two fluids move counter-current. A weight of hot fluid M_1 of specific heat σ_1 enters at ${}^1\theta_0$ and leaves at ${}^1\theta_1$ undergoing a cooling τ_1 degrees, while a weight of cold fluid M_{11} of specific heat σ_{11} enters at ${}^{11}\theta_0$ and leaves at ${}^{11}\theta_1$, changing in temperature by τ_{11} degrees. When the object is to heat the cold fluid, ${}^1\theta_1$ is a variable and it may be made a function of x by placing ${}^1\theta_0 - {}^{11}\theta_1 = \Delta$ and ${}^1\theta_1 - {}^{11}\theta_0 = \Delta x$.

Then,

$$\Delta_m = \Delta \sqrt{x} \text{ or } \Delta \frac{x-1}{\ln x}$$

$$M_1 = \frac{Q}{\sigma_1(\Delta - \Delta x + \tau_{11})} \text{ and } A = \frac{Q}{\Delta_m T_g}$$

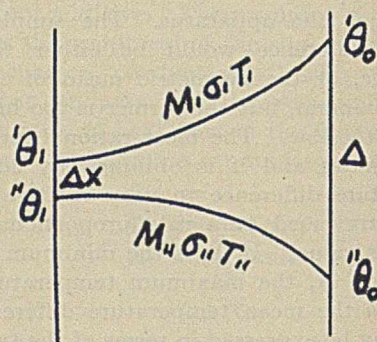
Q is the total heat to be transferred and $Q = M_1 \sigma_1 \tau_1 = M_{11} \sigma_{11} \tau_{11}$ neglecting outside radiation losses

When the object is to cool the hot fluid, ${}^{11}\theta_1$ is the variable and $x = \frac{{}^1\theta_0 - {}^{11}\theta_1}{{}^1\theta_1 - {}^{11}\theta_0}$, $\Delta = {}^1\theta_1 - {}^{11}\theta_0$.

Then,

$$\Delta_m = \Delta \sqrt{x} \text{ or } \Delta \frac{x-1}{\ln x}$$

$$M_{11} = \frac{Q}{\sigma_{11}(\Delta - \Delta x + \tau_1)} \text{ and } A = \frac{Q}{\Delta_m T_g}$$



Parallel current heat transfer is graphically presented above. When the object is to heat the cold fluid, ${}^1\theta_1$ is variable; to cool the hot fluid, ${}^{11}\theta_1$ is variable. Then,

$$\Delta_m = \Delta \frac{x-1}{\ln x}$$

$$M_1 = \frac{Q}{\sigma_1(\Delta - \Delta x - \tau_{11})} \text{ or}$$

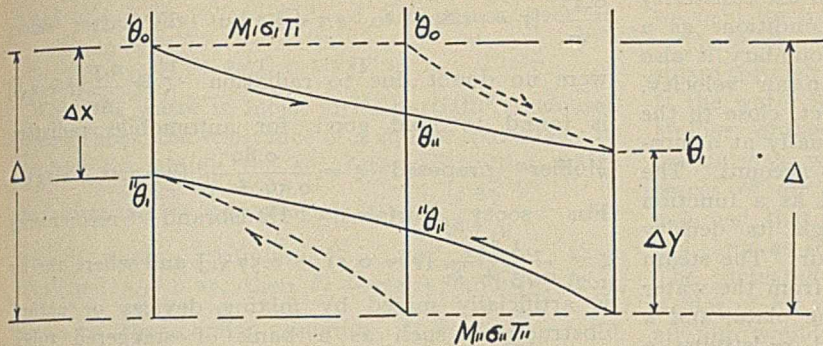
$$M_{11} = \frac{Q}{\sigma_{11}(\Delta - \Delta x - \tau_1)} \text{ and } A = \frac{Q}{\Delta_m T_g}$$

In perpendicular current heat exchange, a hot fluid of weight M_1 , specific heat σ_1 , enters at ${}^1\theta_0$ and is cooled to a temperature ranging from ${}^1\theta_1$ to ${}^1\theta_1$, and undergoing a mean change of temperature τ_1 . A cold fluid of weight M_{11} , specific heat σ_{11} , enters at ${}^{11}\theta_0$ and is heated to temperatures ranging from ${}^{11}\theta_{11}$ to ${}^{11}\theta_1$, and undergoing a mean temperature increase of τ_{11} degrees. As before, $Q = M_1 \sigma_1 \tau_1 = M_{11} \sigma_{11} \tau_{11}$.

$$\text{Let } x = \frac{{}^1\theta_0 - {}^{11}\theta_1}{{}^1\theta_1 - {}^{11}\theta_0} \text{ and } y = \frac{{}^1\theta_1 - {}^{11}\theta_0}{{}^1\theta_0 - {}^{11}\theta_0}$$

Then,

$$\Delta_m = \Delta \sqrt{xy} \text{ or } \Delta \frac{x-1}{\ln x} \cdot \frac{y-1}{\ln y}$$



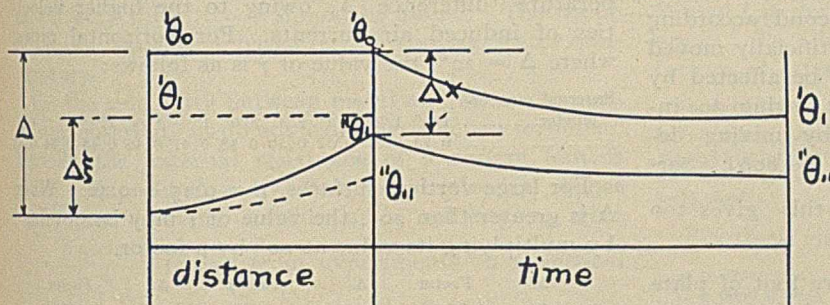
Assuming θ_{11} , θ_1 and θ_{11} , θ_{11} straight lines, which is approximately true, then,

$$M_{11} = \frac{2Q}{\sigma_1 [\Delta(3-x-y-xy) - 2\tau_{11}]} \text{ or}$$

$$M_{11} = \frac{2Q}{\sigma_{11} [\Delta(3-x-y-xy) - 2\tau_{11}]}$$

and

$$A = \frac{Q}{\Delta_m T_g}$$



In a single current apparatus for cooling, a hot fluid is cooled from θ_0 to θ_1 . It is here assumed that the temperature of all parts of the fluid that remains in the apparatus during the operation is the same at any time, owing to the use of good stirring devices. The cold fluid enters at θ_0 and is heated at first to θ_{11} , finally to θ_{11} undergoing a mean temperature rise of τ_{11} degrees. Again, $Q = M_{11}\sigma_1\tau_{11} = M_{11}\sigma_{11}\tau_{11}$. Assuming the curve θ_{11} , θ_{11} a downward parabola, then,

$$\Delta_m = \Delta \sqrt{x\xi} \text{ or } \Delta \frac{x-1}{\ln x} \cdot \frac{\xi-1}{\ln \xi}$$

$$M_{11} = \frac{3Q}{\sigma_{11}\Delta(1+2\xi)(1-x)} \text{ and } A = \frac{Q}{\Delta_m T_g}$$

For an extended mathematical study of problems of this type, the reader is referred to papers by M. Berlowitz, "Beitrag zur Berechnung der Heizflächen," *Zeitschrift fur Apparatentechnik*, 1908.

In the design of apparatus, no data as to conductivity values is as valuable to the engineer as those obtained by experiment on similar apparatus under exactly the same working conditions. Such data may, however, be found rare, and if all conditions do not coincide, it may be misleading. Such data, if used, ought to be carefully analyzed into its essential parts. In the lack of such data, resource must

be had to what few values, formulae, and rules are extant on the subject, and by careful piecing together of the same, results of no great engineering inaccuracy may be obtained.

The internal conductivity values for different materials has been subjected to much more accurate determinations than boundary conductivities. The internal conductivity is affected by but one variable temperature; the effect of this is but slight, and need not be taken into account.

Below is given a few values of λ and ρ in pound, inch, square foot, hour units.

	λ	ρ
Silver.....	3180	0.00031
Copper ¹	3020-2660	0.00033-0.00038
Aluminum.....	1000	0.001
Zinc ¹	880	0.0011
Tin ¹	435	0.0023
Wrought iron.....	450-420	0.0022-0.0024
Cast iron ¹	490-310	0.0020-0.0032
Steel ¹	320-180	0.0031-0.0056
Lead ¹	230	0.0044
Boiler scale ²	22-8.8	0.05-0.11
Marble.....	14.5	0.07
Glass.....	7.2	0.14
Water.....	4	0.25
Glycerin.....	2	0.5
Alcohol.....	1.1	0.9
Ether.....	0.9	1.1
Oil ²	0.8	1.3
Air.....	0.16	6.3
Carbon dioxide ..	0.1	10

Another table given by Lamb and Wilson may be added, although it corroborates certain values given above.

	λ	ρ
Aluminum.....	995-1005	0.001
Brass.....	590-735	0.0017-0.0014
Copper.....	2085-2095	0.00048
Iron.....	480-470	0.0021
Lead.....	245-220	0.0043
Tin.....	445-315	0.00225-0.00415
Zinc.....	880	0.0012
Clay slate.....	7.9	0.12
Granite.....	14.8-16.0	0.065
Marble.....	13.6-16.3	0.07
White dry sand.....	2.7	0.37
Compact sand.....	1.48	0.68
Plaster of Paris.....	3.7	0.26
Pasteboard.....	1.3	0.77
Fir (along grain).....	0.87	1.15
Fir (across grain).....	0.26	3.9
Hair felt.....	0.31-0.42	2.8
Charcoal.....	0.44	2.3
Silicate cotton.....	0.44	2.3
Brown paper.....	0.48	2.1
Pine shavings.....	0.47	2.1
Air (no baffles).....	0.57	1.75
Pure sawdust.....	0.70	1.4
Dry asbestos.....	0.86	1.15
Sand.....	2.15	0.47

Boundary resistivity is very difficult to express in terms of formulae or equations, owing to the number of factors upon which it depends. The resistivity of a water boundary is usually expressed as a function of the mean velocity of the water where that velocity

¹ *Zeitschrift des Vereines deutscher Ingenieure*, 1876.

² W. Ernst, *Kaiserliche Akademie des Wissenschaften*, 1902.

is artificially impressed, but where the water is "still," it is not so expressed. The resistivity of denser and more viscous liquids is often referred to the resistivity that water would have under like conditions as a standard. The resistivity of an air boundary is also expressed as a function of the mean air velocity, but the air density has a marked effect, close to the inverse of its cube root. As air is usually at atmospheric pressure, this is not taken into account. The heat resistivity of steam is expressed as a function of its mean initial velocity, although its density has an effect much the same as with air. The steam resistivity is not commonly separated from the water resistivity on the opposite side of the plate, and a favorite formula makes the external resistivity a function simply of the plate or tube area. Finally, to allow for incrustation, heat resistance of the metal, oily surface, etc., a factor is often applied to the external resistance. A more rational way is to add the heat resistance of a known thickness of metal, plus the heat resistance of an assumed thickness of scale and oil onto the external resistance.

Between metal and water, the resistivity $\zeta = \frac{0.005}{0.3 + \sqrt{v}}$ [$\gamma = 60 + 200\sqrt{v}$] where v is the velocity of the water in feet per second according to Mollier.¹ When the water is not artificially moved $\zeta = 0.01$ [$\gamma = 100$], although this will be affected by the temperature difference somewhat, owing to induced currents. For water stirred by mixing devices, $\zeta = 0.0025 - 0.0013$ [$\gamma = 400 - 800$]. Ser² places $\zeta = \frac{0.002}{\sqrt{v}}$ [$\gamma = 500\sqrt{v}$], but this gives too high a flow of heat.

The external resistance z_0 of a square foot of plate with moving on both sides is the sum of the separate boundary resistivities.

$$z_0 = \frac{0.005}{0.3 + \sqrt{v_1}} + \frac{0.005}{0.3 + \sqrt{v_{11}}}$$

v_1 and v_{11} are the respective velocities of the water on either side.

To obtain z , the internal resistance of a square foot $\delta\rho + \delta_1\rho_1$ may be added to z_0 , where δ and δ_1 are the thicknesses of metal and maximum allowable thickness of incrustation in inches, and ρ and ρ_1 are the respective resistivities. Practical rules given by Hausbrand³ are that z may be obtained by multiplying z_0 by 1.5 for copper or brass pipes, by 2.0 for iron pipes, and further this should be multiplied by 1.33 where thick liquids are heated, by 1.33 if the surface is oily, and by 1.66 for very thick liquids.

When water is being evaporated by a hot high boiling liquid moving at a velocity v ,

$$z_0 = \frac{0.045}{\sqrt{v}} [g_0 = 22\sqrt{v}].$$

When air is heated by hot water or steam pipes, the air boundary resistance is so large that in comparison the other resistances become negligible;

hence, $\zeta = z_0 = z$. Joule¹ states that $\zeta = \frac{0.55}{\sqrt{v}}$ to $\frac{0.47}{\sqrt{v}}$ [$\gamma = 1.8\sqrt{v}$ to $2.1\sqrt{v}$], but the latter values

were no doubt due to radiation. $\zeta = \frac{0.5}{\sqrt{v}}$ [$\gamma = 2\sqrt{v}$] is found to hold good for automobile radiators.

Mollier² proposed $\zeta = \frac{0.89}{0.36 + \sqrt{v}}$ [$\gamma = 0.41 + 1.13\sqrt{v}$]. For sooty surfaces, Hausbrand recommends

$\zeta = \frac{1.77}{0.73 + \sqrt{v}}$ [$\gamma = 0.41 + 0.57\sqrt{v}$] and where the air is artificially mixed by mixing devices or natural obstructions such as a bank of staggered tubes,

$\zeta = \frac{1.08}{0.45 + v^{\frac{1}{3}}}$ [$\gamma = 0.41 + 0.92v^{\frac{1}{3}}$]. Experiments by

E. Josse, of Charlottenburg, on air moving inside of tubes, give $\zeta = \frac{1.6}{v^{\frac{1}{3}}}$ [$\gamma = 0.63v^{\frac{1}{3}}$] at atmospheric pressure, but with a lower constant for lower pressures.

When air is not artificially moved, the empirical observations of Peclet may advantageously be employed.

The value of γ is found to increase with the temperature difference Δ , owing to the higher velocities of induced air currents. For horizontal pipes, where $\Delta = 20^\circ$, the value of γ is as follows:

External pipe diameter.....	1/6"	1/2"	1/2"	2/3"	5/6"	1"	1 1/2"	2"	3"	4"
γ	0.73	0.57	0.52	0.50	0.48	0.47	0.46	0.45	0.44	0.43

For large vertical surfaces, $\gamma = 0.45 - 0.40$. When Δ is greater than 20° , the value of γ may be obtained by multiplying its value at 20° by a factor.

Δ .	Factor.	Δ .	Factor.	Δ .	Factor.
20	1.00	225	1.69	425	1.97
50	1.22	250	1.73	450	2.00
75	1.31	275	1.77
100	1.40	300	1.81
125	1.47	325	1.85
150	1.53	350	1.88
175	1.58	375	1.91
200	1.64	400	1.94

The resistance of a square foot of pipe where heat travels from air through the pipe to air, where v_1 is the velocity of the air inside of the pipe and v_{11} is the velocity of the air outside of the pipe, may be found from either of the following equations:

$$Z = \frac{1.6}{v_1^{\frac{1}{3}}} + \frac{0.89}{0.36 + v_{11}^{\frac{1}{3}}} \quad (1)$$

$$Z = \frac{1.6}{v_1^{\frac{1}{3}}} + \frac{1.08}{0.45 + v_{11}^{\frac{1}{3}}} \quad (2)$$

In (1) the air outside moves parallel to the pipe and in (2) the outside air moves perpendicularly against staggered pipes.

From water to air $\zeta = \frac{1.08}{0.20 + \sqrt{v}}$ [$\gamma = 0.41 + 2.04\sqrt{v}$] where v is the velocity of the air and the water is broken up into drops as in open-air coolers. When the water is allowed to flow evenly over vertical or

¹ *Zeitschrift des Vereines deutscher Ingenieure*, 1897.

² *Physique industrielle*.

³ *Verdampfen, Kondensieren, and Kühlen*.

¹ *Philosophical Transactions of the Royal Society*, 1861.

² *Zeitschrift des Vereines deutscher Ingenieure*, 1897.

sloping surfaces $\zeta = \frac{0.75}{0.36 + \sqrt{v}} [\gamma = 0.41 + 1.33\sqrt{v}]$.

When the water is still and air passes over it,

$$\zeta = \frac{0.89}{0.36 + \sqrt{v}} [\gamma = 0.41 + 1.13\sqrt{v}]$$

When the water in moist air is partially condensed by cold tubes, the resistance of a square foot z may be obtained by adding the separate resistivities which

are (1) from water to moving air, $\zeta = \frac{0.89}{0.36 + \sqrt{v_1}}$; (2)

through water, assuming δ is not greater than $1/10''$ and $\rho = 0.25$, then $\delta\rho = 0.025$; and (3) from

metal to the cooling medium, $\zeta = \frac{0.005}{0.3 + \sqrt{v}}$ for

water and $\zeta = \frac{1.6}{v_{11}^3}$ for air.

Occasionally, liquids are cooled by flowing over metallic pipes cooled internally by water. The outside air effects cooling both by assisting evaporation and by conduction. For copper or brass pipes, $z = 0.005$ when the temperature of the liquid to be cooled is above $60^\circ F.$, 0.006 when at $60^\circ F.$ and 0.007 when below $60^\circ F.$ If the metal is iron 0.001 should be added; if the liquid is thicker than water 0.001 , and if very thick, 0.002 should be added. The value of Δ_m in this case is based on the cooling water temperatures.

On the resistivity between metal and steam, experimental observations do not lead to satisfactory formulae. Usually the external resistance of a square foot is given. Experiments by Ser¹ on horizontal tubes with water moving outside at a velocity v_{11} give

$z_o = \frac{0.0022}{v_{11}^3}$. Joule,² from experiments on a vertical

tube of small diameter, found $z_o = \frac{0.0042}{v_{11}^3}$. Nichol³

found the ratio of z_o of a vertical tube to z_o of a horizontal tube to be $1^2/2$, but he obtained a higher value for z_o than Ser. Hagerman⁴ found the rate of heat transmission to depend on the temperature of the water and steam. If t is the steam temperature plus the average water temperature divided by 180, then,

$$z_o = \frac{0.0088}{1 + t} \cdot \frac{0.091}{1 + t + \sqrt{v_{11}}}$$

According to the observations of Hausbrand, if v_1 is the mean initial steam velocity, and v_{11} is the mean water velocity, then,

$$z_o = \frac{0.0175}{v_1^3 \sqrt{0.023 + v_{11}}}$$

To obtain z add $\delta\rho + \delta_1\rho_1$. For iron pipes, multiply by 1.33.

Where water is pumped through coils surrounded by steam, $z_o = \frac{0.0096}{\sqrt{0.023 + v_{11}}}$ where v_{11} is the velocity

of the water; $z_o = \frac{0.04}{v_1^3}$ to $\frac{0.02}{v_1^3}$ where liquids are warmed up by steam coils without stirring.

These formulae deal with the resistivity from steam through plates to water which is not evaporating. If the water is boiling, other formulae must be used. Mollier obtained $z_o = 0.0014$, but where rigorous precautions were employed to completely exclude traces of air from the steam, $z_o = 0.0007$. Mollier assumed that the resistivity from metal to water is the same as from metal to steam, $\zeta_1 = \zeta_{11} = 0.00035$. The increased resistance is believed to be due to a film of air. The resistance of a square foot of an air film would be 0.001 on this assumption, and since the heat resistivity of air is 6.25 the film thickness would be $0.0002''$.

From experiments on evaporation, Jellinck¹ proposed the following formula, expressing the resistivity in terms of c the circumference of the steam pipe in feet, and l its length in feet, or A the area in square feet.

$$z_o = 0.00045c^2 l^2 = 0.00045 \sqrt{Al} g_o = \frac{2200}{\sqrt{A}}$$

Actually, l does not vary as l^2 but as l^2 to l^3 . Where l is very large or small this formula does not apply. To allow for incrustation, etc., the following factors of safety are recommended by Hausbrand.²

Ratios of z/z_o .	Water.	10-25% solid.	Viscous liquids.
Copper tubes.....	1.5	2.0	2.5
Wrought iron tubes.....	2.0	2.5	3.0
Cast iron tubes.....	2.5	3.3	4.0
Lead pipes.....	3.0	4.0	4.5

For thick viscous liquids:

- $z = 0.075-0.0065$ long heating coils.
- $= 0.0060-0.0055$ short heating coils.
- $= 0.0050$ thin heating coils.
- $0.0070-0.0080$ vertical systems of tubes with steam outside.

In vacuum evaporators, the resistance may become 1.2 to 1.5 times that given above.

In the case of steam-jacketed kettles, if Δ is the temperature difference between the evaporating liquid and the initial steam temperature, then Δ_m should be chosen less than $\frac{1}{2}\Delta$ as is given in the following table:

Diameter of kettle.	z_o .	Δ_m/Δ .
Up to $2\frac{1}{2}'$	0.0027	0.85
$2\frac{1}{2}'-5'$	0.0029	0.80
$5'-7\frac{1}{2}'$	0.0031	0.75
$7\frac{1}{2}'-10'$	0.0033	0.70
10' and over.....	0.0035	0.65

For iron, $\frac{z}{z_o} = 1.33$. If there are two steam openings this should be multiplied by $3/4$, for four steam openings multiply by $2/3$, and if a stirring apparatus is used $1/2$ should be used to multiply with.

For vacuum steam-jacketed kettles:

- $z = 0.0040-0.0048$ water.
- $= 0.0048-0.0055$ thin liquid.
- $= 0.0055-0.0100$ thick liquid.

Where multiple-effect evaporators working on liquors presenting no special difficulties, ordinary depths

¹ Zeitschrift des Vereines für Rubenzucker Industrie, 1894.

² Verdampfen, Kondensieren, and Kühlen, 1909.

¹ Physique industrielle.

² Philosophical Transactions of the Royal Society, 1861.

³ Engineering, 1875.

⁴ Proceedings of the Institute of Civil Engineers, 1844.

of liquor being maintained and heated by brass tubes of three feet or over in length, the values of

$$\Delta g = \frac{Q}{TA} \text{ are as follows:}$$

Single effect.....	14000-16000 B. t. u. per sq. ft. per hour
Double effect.....	6000- 7500 B. t. u. per sq. ft. per hour
Triple effect.....	4000- 5200 B. t. u. per sq. ft. per hour
Quadruple effect.....	3750- 4400 B. t. u. per sq. ft. per hour

Where the depth is lower than usual these figures are 10 per cent. higher, wide horizontal tubes 10 per cent. more, narrow, horizontal tubes 15 per cent. more, iron horizontal tubes 10-15 per cent. less, and for evaporators of the spraying or showering types, 10 per cent. more.

THE UTILITY OF THE METALLOGRAPHIC MICROSCOPE.

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Received April 22, 1911.

This article will be confined entirely to the metallographic microscope, without touching upon its use in the immense fields of geology and botany, where the examination of rock sections and vegetable products has a direct utility in engineering. Here, however, the methods are somewhat different than in metallography, since transparent sections and transmitted light (often polarized light) are used. Also, it is not purposed to dwell especially upon the technique of microscopic metallography. The methods employed are presented in good form in several books and numerous articles devoted to the subject. Again no detailed or elaborated discussion of any complex phase of the subject will be taken up. Rather, concrete examples will be brought forward illustrating what metallography has done for us, with the hope that the discussion will open suggestions of its possibilities in individual fields of endeavor.

Metallography is but a step towards the rationalizing of our study of metals and alloys. The earlier work in the study of these materials was naturally along the lines of their possible uses; it consisted of tests of these various properties and a classification according to their several fields of service. A vast accumulation of data of this kind led to the adoption of a rather empirical correlation of composition and quality. Chemical analysis later came in to give us a more exact correlation by the elimination of one big uncertainty, the composition. But chemical analysis falls short of giving us sufficient information regarding our material. Substances owe their properties solely to their make-up, or structure. Composition is but one of the determining factors; chemical analysis therefore fixes but one of the variables. The relation of these chemical elements or the make-up of the material is most vitally dependent on its history. Temperature and pressure conditions, or the proximity of disturbing influences, are of importance. In steels, for example, we consider the effects of heat and mechanical treatment; that is, for identical analyses, a steel annealed at 1200° C. would be weaker than one annealed at 800° C.; one quenched at 800° C. would be harder than the same material slowly cooled from

that temperature, while cast material is weaker than that which has had subsequent rolling or forging.

Structure or make-up is therefore the first step in the interpretation of the properties of materials. An essential in this determination is the composition; chemical analysis is therefore a necessity, and it must be understood clearly that metallographic study is only an auxiliary to the other methods of test. Two lines of attack are open: by the use of the pyrometer and by the use of the microscope. The latter was developed much the earlier, having its beginning in the work of Dr. Sorby in England in 1864 and the later independent investigations of Martens in Germany in 1875. However, the real development has come about within the last ten years; this is due to the rapid progress in physical chemistry, particularly in a better understanding of the theory of solutions. In the earlier work it was possible to develop the structure of the material under examination, but the full measure of the value of the work was missed through the inability to interpret the developments; again systematic research was handicapped by this lack of knowledge. To-day we have a rational interpretation of the results of solidification of molten mixtures and a consequent explanation, more or less developed, of the variations in the structure of alloys occasioned by changes of composition or treatment.

It will be impossible in this paper to dwell upon the use of the pyrometer in the study of the structure of alloys. Cooling curves obtained by its use undoubtedly furnish the most rational basis for the theoretical deductions of the results to be expected on solidification of the melt. But outside of its very direct practical bearing in certain instances, notably in the determination of the critical points of tool steels, the pyrometer may be said in general to be of more scientific interest. The microscope, on the other hand, has a more direct application in the industrial laboratory since with it one is able to make an examination of any desired material as it is used or as it exists, and to interpret from the structure, backed by experience, the condition of the material and its suitability for the purpose in view.

Microscopic examination of metals and alloys is passing through the same cycle that the chemical analysis of iron and steel did some years ago. We have the enthusiast, who would claim for the microscope the power to usurp the functions of other testing methods; and the skeptic, who treats it as a toy and scoffs at any suggestion of utility outside of the laboratory of the scientific investigator. The chief argument of the latter is that the field of view of the microscope is only an extremely small part of a very small sample cut from a large mass of material and it can disclose, therefore, only local conditions. Such argument is hardly tenable; it would apply with equal force to the one-gram sample, the chemical analysis of which controls the 60-ton heat of a steel furnace; or to the purchase of a car-load of coal or a boat-load of ore on determinations of heating value, composition, etc., made on equally small units; or to our methods of design of structures from material whose

strength is taken as that of a small test sample. In fact, all testing methods are based on the principle of a fair average sample of the material under test.

Osmond, the noted French worker, has aptly classed the divisions in the microscopic examination of metals and alloys as anatomical, biological, and pathological. Taking up the last division first, it is needless to point out that the microscope is useful in the detection of incipient cracks and flaws, slag or foreign inclusions, porosities, and the numerous other ills that metals are heir to. Fig. 1 illustrates this point; it is a section of a piece of wrought iron taken perpendicular to the direction of rolling, and shows a slag inclusion. It needs no comment, as it must be very evident that slag particles so breaking the continuity of the metal will have a material effect on the physical properties.

In Fig. 2 is shown a section of a brass casting made in the course of an investigation for a manufacturer who was having trouble with his product. The brasses used were of a composition of about 80 per cent. copper, 10-15 per cent. zinc and 5-10 per cent. lead, the last named being the very common addition agent to brasses to facilitate machining. But brass will hold in solution after solidification only a very small percentage of lead, and any excess will therefore separate out in the free state. This is clearly indicated in the photomicrograph where the free lead is shown in its typical form of black globules. Its effect in machining becomes apparent, since it will break into short chips the otherwise long curling ones of the high copper brasses. On the other hand, it must have equal influence in lowering the strength and ductility of the product; and it is surely not a desirable addition in brasses to be subjected to high temperatures, since the lead will soften or melt at temperatures much below the fusion point of the body material.

Figs. 3 and 4 illustrate a case where the utility of the microscope was rather indirect. Two brass manufacturing concerns A and B were putting on the market a standard article for which there was a large demand. But B's proved stronger than A's and analysis of B's goods indicated the presence of 1 per cent. of iron in the brass. However, when A tried out the new composition it failed to give the strength of B's. Although the compositions are identical the structure differences are pronounced, as indicated in Fig. 3 (of A's) and Fig. 4 (of B's). The coarse structure of A's, together with its marked dirtiness and porosity as compared with the other, led to further investigation, with the final development that the 1 per cent. of iron in B's product had little direct bearing on the strength, and was only that something which was inevitably left behind on the addition of ferromanganese to deoxidize the bath, the manganese being slagged off, and the brass casting left with a clear, fine-grained structure of great strength.

The most work with the microscope has been done in the anatomical division, in the determination of the inner make-up of metals and alloys. Use is made of three facts so fundamental and so vital that they may be presented as axioms.

(1) Metals and alloys are crystalline.

(2) The structure is homogeneous or heterogeneous. Solubility relations govern. It is homogeneous in pure substances, in solid solutions, or in the metallic compounds, and heterogeneous if there is no solubility, or only partial solubility of the constituents after solidification.

(3) The individual melting points of the constituents have no bearing on the order of their crystallization from the melt. The solubility relation of the constituents is again the governing factor.

Fig. 5 is a photomicrograph of Swedish iron and shows the typical homogeneous structure and crystalline habit of a pure metal. The irregular boundaries of the grains are not due to the crystal faces, but indicate rather that crystallization has proceeded from nuclei, or centers, with varying rates of speed, and that the limit of growth has been that due to interference by an adjoining grain. Each grain is a crystalline aggregate of definite crystal system and uniform orientation.

The heterogeneous structure of certain alloys is illustrated in Figs. 6, 7 and 8, the sections being a series of lead-antimony alloys of compositions respectively of 50 Sb, 50 Pb; 13 Sb, 87 Pb; and 5 Sb, 95 Pb. This series is of the type of alloys where the solubility is *nil* after solidification, with consequent complete separation of the constituents as shown, the white being the antimony and the black the lead. In this series, the antimony freezes at 632° C. and the lead at 326° C. and we might expect, therefore, that the antimony would always crystallize out first in a matrix of still fluid lead. This is far from the facts, however, and we see in Fig. 6 the excess antimony crystallizing in a matrix of the eutectic of antimony and lead; in Fig. 8 the lead has solidified first in its typical form in the same matrix as before; while in Fig. 7 we have the eutectic, with its finely divided, intimate mixtures of lead and antimony, due to solidification together at a constant temperature of 228° C. or about 100° C. below the freezing point of the more fusible constituent.

Advantage is taken of this selective crystallization in bearing metals. While suitable bearing metals had been made long before metallography came to our aid, it has pointed out the reasons for success in the use of certain mixtures, and the line of attack necessary in looking for new ones. There are two chief desiderata for a bearing material: First, a low coefficient of friction; this is lowest with the hard metals. Second, plasticity, in order that as unequal wear occurs the pressure of the shaft will squeeze the bearing into conformity and thus avoid local heating by distributing the load equally over the entire surface; this plasticity is obtained with soft materials. Two such opposite properties, hardness and softness, are manifestly not to be obtained by the use of any single homogeneous substance. But by taking advantage of the selectiveness of freezing, we can obtain alloys in which we have a hard constituent bedded in a plastic matrix; the exact nature of the alloy will, of course, depend upon the character of service and the

amount of unit stress on the bearing material. One of our common alloys, Magnolia metal, is of the lead-antimony series, carrying about 20 per cent. of antimony, and consisting therefore of antimony crystals bedded in a plastic eutectic of lead and antimony. Its microstructure would be intermediate between those shown in Figs. 6 and 7.

In Fig. 9 is shown the structure of a Babbitt metal of the copper-tin-antimony series with two hard constituents, the cubes of $SbSn$ and the needles of $SnCu_3$, bedded in the backing of copper.

All of our bearing materials, including Babbitt metals, machinery brasses and bronzes, and cast iron, may be shown to fulfil the conditions laid down above.

In no field is greater use made of the properties resulting from selective freezing than in the ordinary carbon steels. Figs. 10-15 give the structures of several steels with carbon percentages of 0.10, 0.30, 0.60, 0.93, 1.46, and 1.80. We note, as the percentage of carbon increases, that the relative area of the black constituent, as compared to the white, becomes greater, until in Fig. 13, with 0.93 per cent. C., the entire field is occupied by the black constituent. Above this holding of carbon, the white areas increase in magnitude. Structurally, these photomicrographs mean that our slowly cooled carbon steels are heterogeneous, and composed of two constituents, iron (ferrite) and combined carbon (cementite). They are, therefore, made up of an excess substance, either ferrite or cementite, depending upon whether the total carbon is below or above 0.90 per cent., together with the eutectoid of the two constituents, and technically called the pearlite.

In the greatest proportion of commercial steels, with a carbon content below 0.90 per cent., the structure is a heterogeneous mixture of ferrite and pearlite, with the pearlite containing all of the carbon in the form of Fe_3C , the amount of the pearlite increasing as we approach the eutectoid proportion at 0.90 per cent. C. Three facts form the basis of selection of steels of varying carbon percentages for different classes of service; namely, cementite or combined carbon (Fe_3C) is hard, brittle, and of high strength; ferrite, or iron, is soft, ductile and relatively weak; and by shift of carbon composition we can manipulate the relative proportions of these constituents.

In structural steels, with comparatively steady load, we require reasonable strength and elastic limit and high ductility and softness; micrographically, therefore, we need much iron plus some combined carbon, or much ferrite plus some pearlite, which is obtained with a steel of about 0.20 per cent. carbon.

In rails, on the other hand, the load is in the form of a shock, with heavy stresses for short intervals; the requirements are high strength and high elastic limit with reasonable ductility and hardness to resist abrasion. Micrographically this means much combined carbon + some iron, or much pearlite + some ferrite. In open-hearth rails, therefore, we can use steels with carbon from 0.60-0.70 per cent.; but if, because of the irregularities occasioned in manufacture, as in the Bessemer process, we cannot utilize

to the full the properties of the pearlite, we cut the carbon to 0.50 or 0.60 per cent., and reduce the risk of breakage by obtaining higher ductility at the sacrifice of hardness and elasticity.

In line with the above discussion, the microscope shows (Fig. 16) that white cast iron is in reality a very high-carbon steel, with an excess cementite occupying about half of the total field, because of the total carbon content of from $3\frac{1}{2}$ -4 per cent. And we must expect this material to be very hard and brittle and exhibit the silvery fracture from which it derives its name, since the fracture is necessarily along the line of least resistance, or through the brittle cementite areas.

Chemical analysis indicates that gray cast iron differs from the white cast iron not in the quantity of total carbon carried, but because in the gray iron this carbon is largely in the form of free graphite. A simple fracture test shows this, in that a break along the line of least resistance exposes the dark graphite cleavage; hence, the name gray iron. Microscopic examination confirms this, and the distribution of this graphite is shown in Fig. 17 in its typical form as flakes or sheets disseminated throughout the mass of metal. Is it any wonder that cast iron is brittle and weak in tension, when the effective area of the metal is so reduced by the weak plates of graphite? On the other hand, the very thinness of the flakes, while having a maximum effect in lowering the resistance to tensile stress, accounts for the high resistance of cast irons to direct compression. The plates are already so thin that their interposition in the body metal does not result in any further yielding to a direct compressive load.

Except for its free graphite, gray cast iron is seen to be (Fig. 18) nothing more than a steel matrix of high, medium or low carbon, depending upon what proportion of the total carbon has been converted into free graphite because of slow cooling or the presence of silicon or analogous elements.

The microscope is of service in indicating the physical changes taking place in the conversion of hard, brittle white cast iron into the relatively soft and ductile product which we know as malleable cast iron. Due to heat alone (the annealing) the combined carbon is decomposed to iron (ferrite) plus graphite. But since the temperature of annealing is well below that of fusion, the graphite is not free to assume its normal crystalline form (the flake or sheet) and is forced by the comparative rigidity of the metal to assume that shape which will enclose the greatest volume with the minimum of surface. We find the body of the malleable casting to be composed of globules of amorphous carbon bedded in a matrix of iron (Fig. 19). Also, in the usual practice of annealing in mill scale, or its equivalent, the surface layer is decarbonized, to an amount and to a depth depending upon the time, temperature and oxidizing conditions, and appears in the photomicrograph in the typical structure of a carbon-steel. Thus the malleable casting consists of a steel shell of great strength, together with a center of iron in which is embedded graphite in such form as

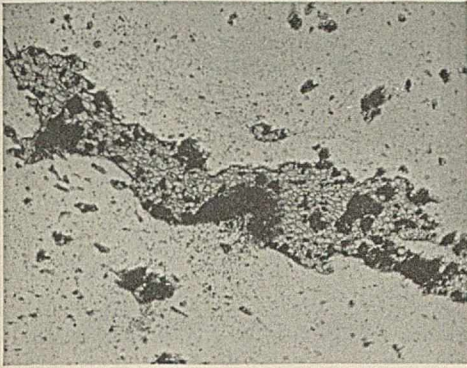


Fig. 1.

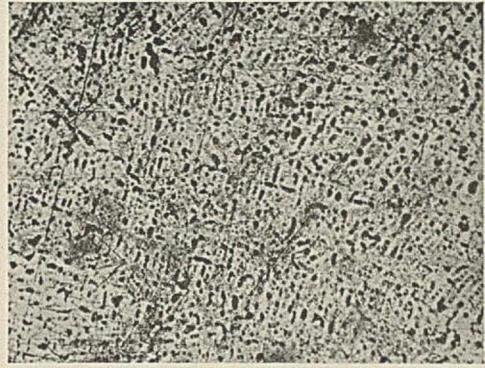


Fig. 2.

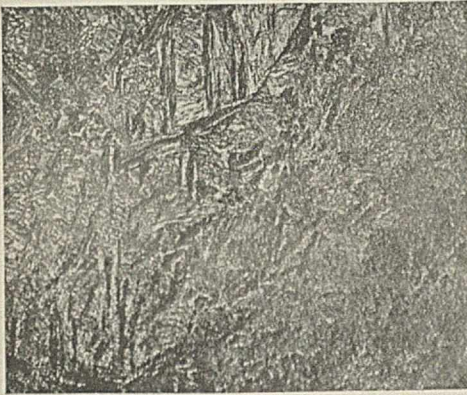


Fig. 3.

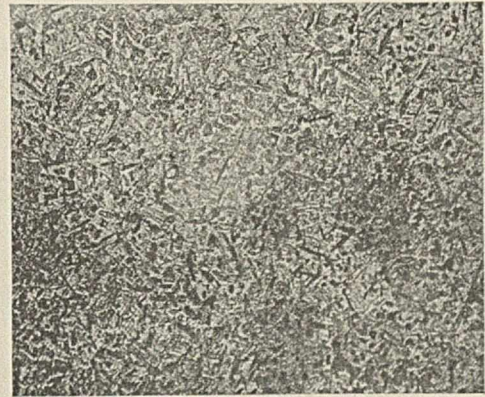


Fig. 4.

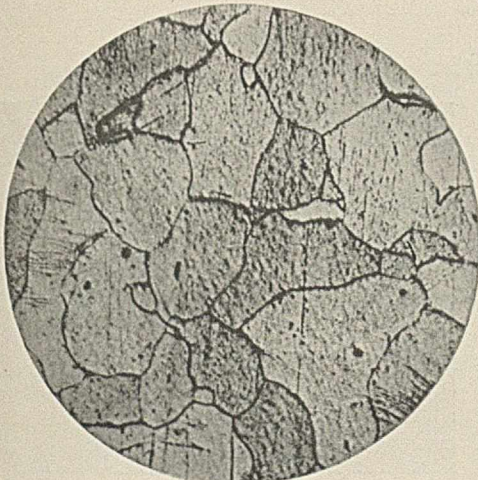


Fig. 5.

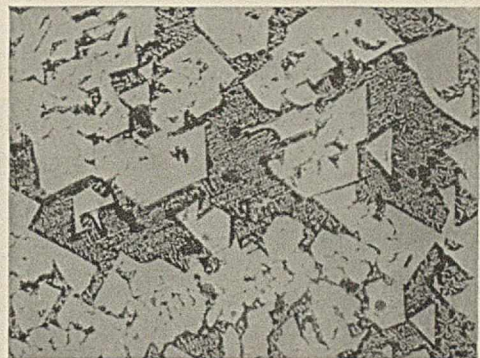


Fig. 6.

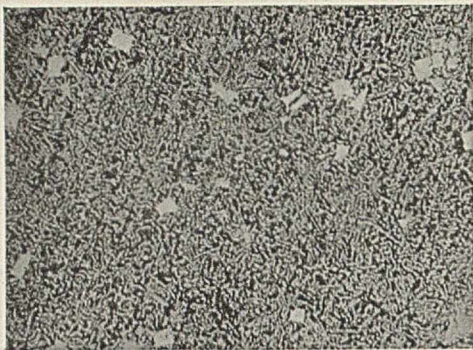


Fig. 7.

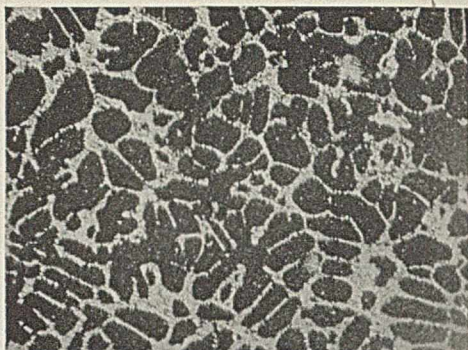


Fig. 8.



Fig. 9.



Fig. 10.

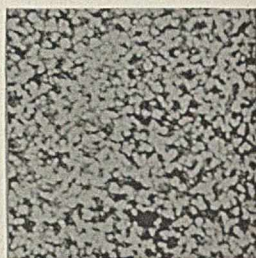


Fig. 11.

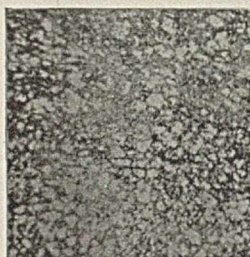


Fig. 12.



Fig. 13.



Fig. 14.

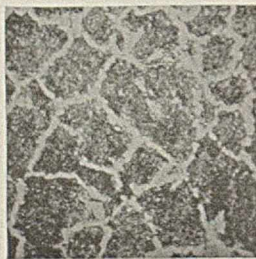


Fig. 15.



Fig. 16.

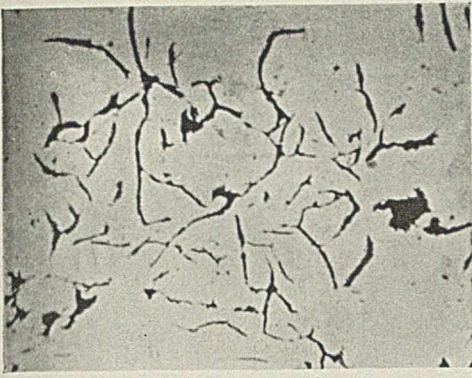


Fig. 17.

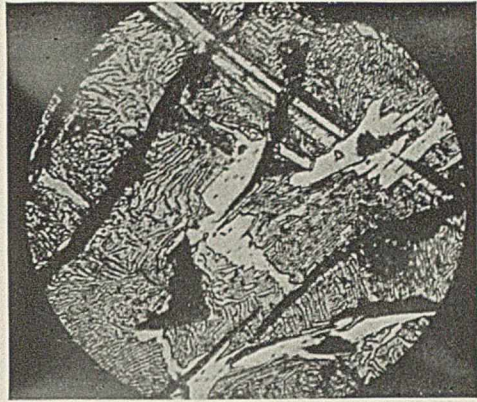


Fig. 18.

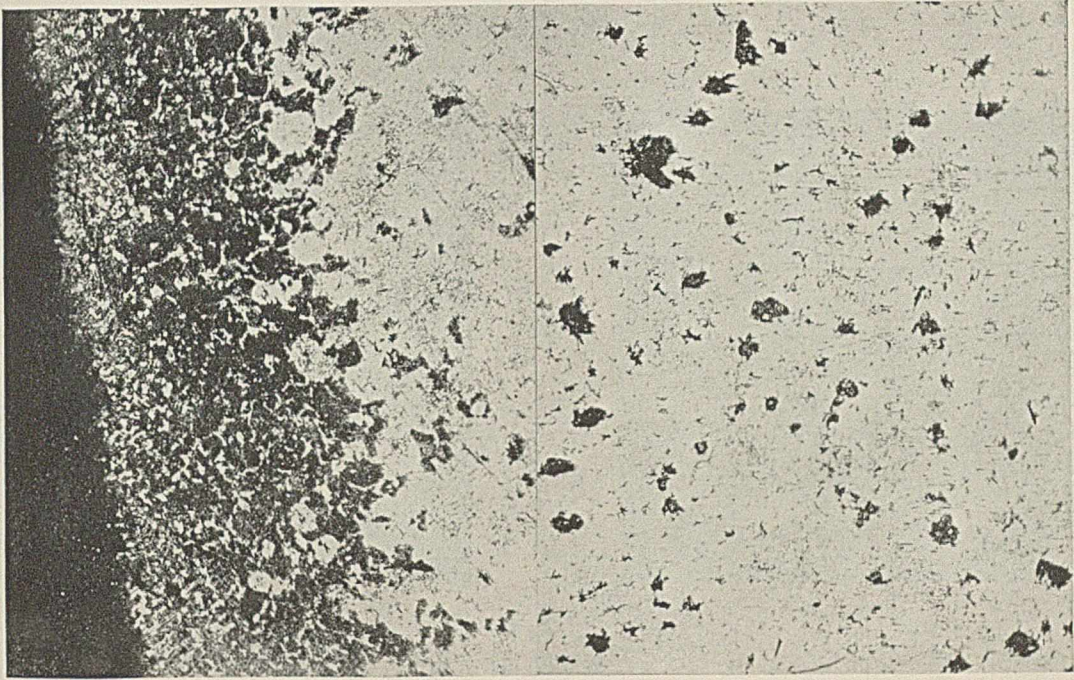


Fig. 19.

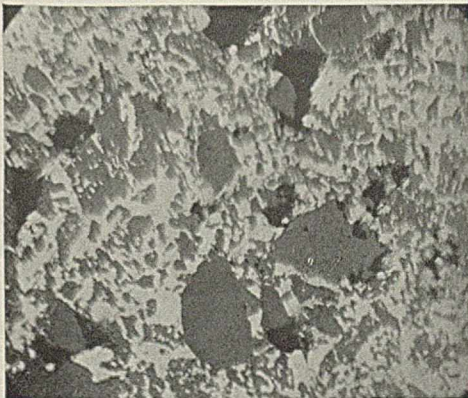


Fig. 20.

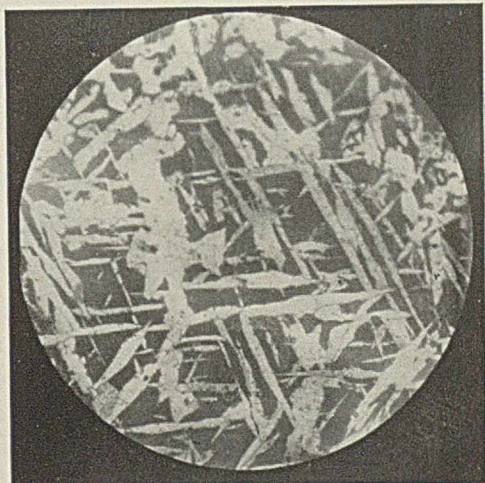


Fig. 21.

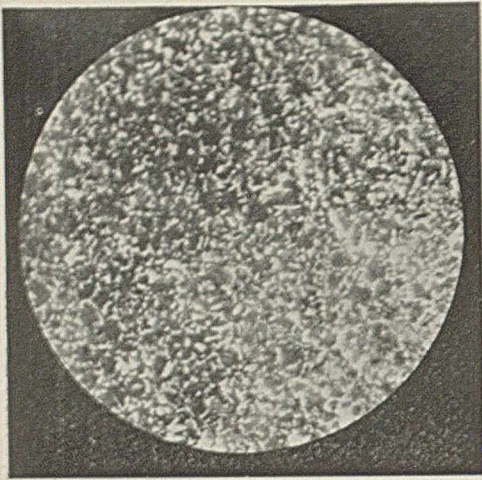


Fig. 22.

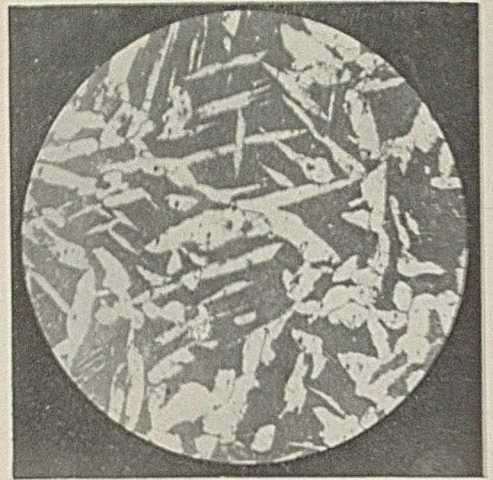


Fig. 23.

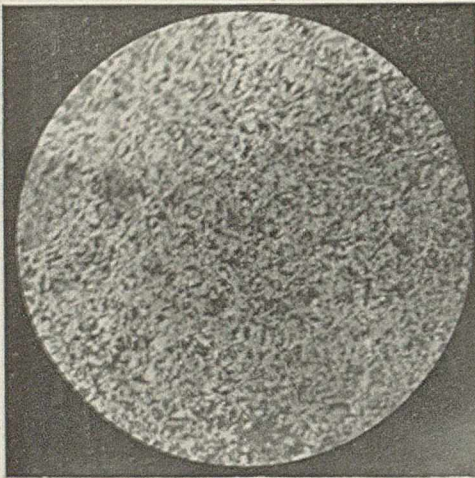


Fig. 24.

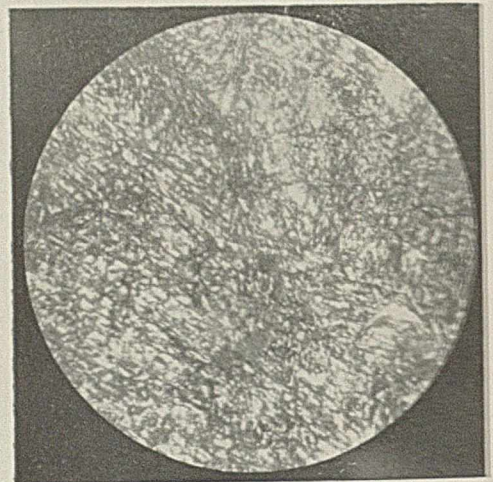


Fig. 25.

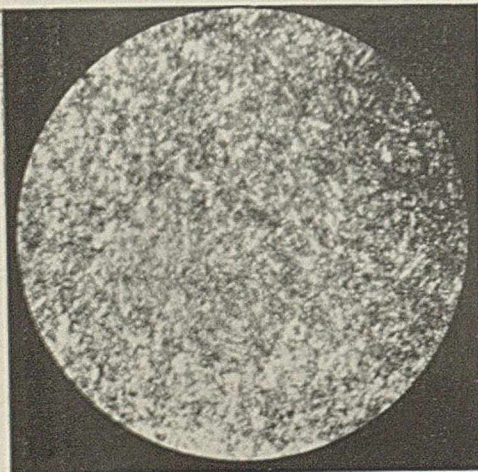


Fig. 26.

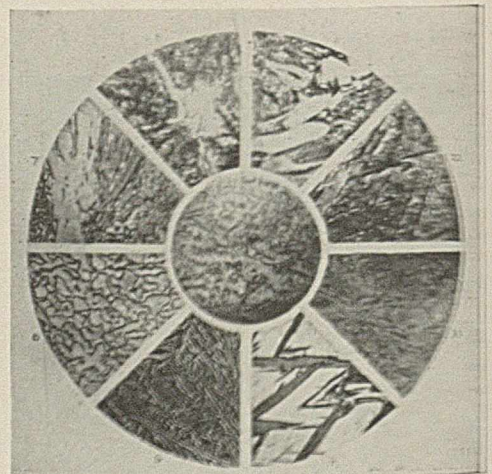


Fig. 27.

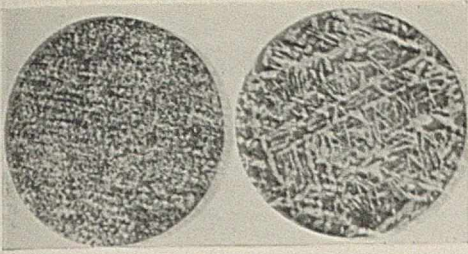


Fig. 28.

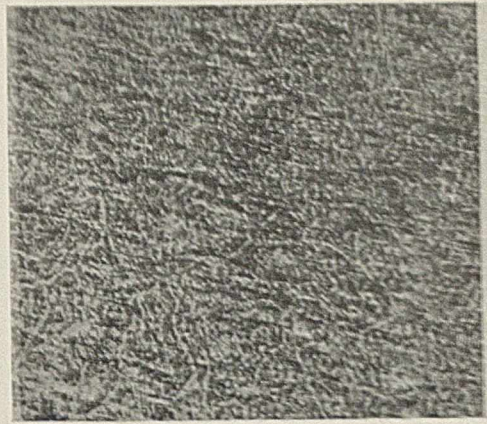


Fig. 29.

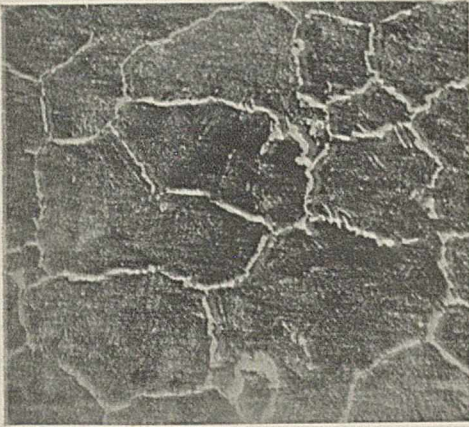


Fig. 30.

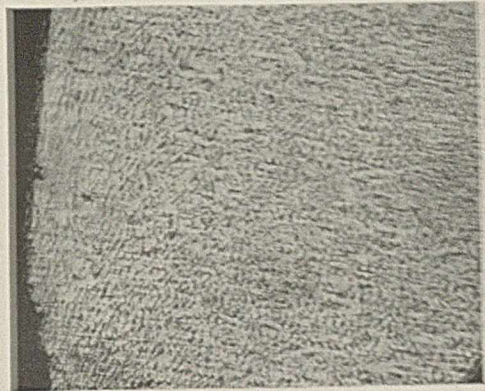


Fig. 31.

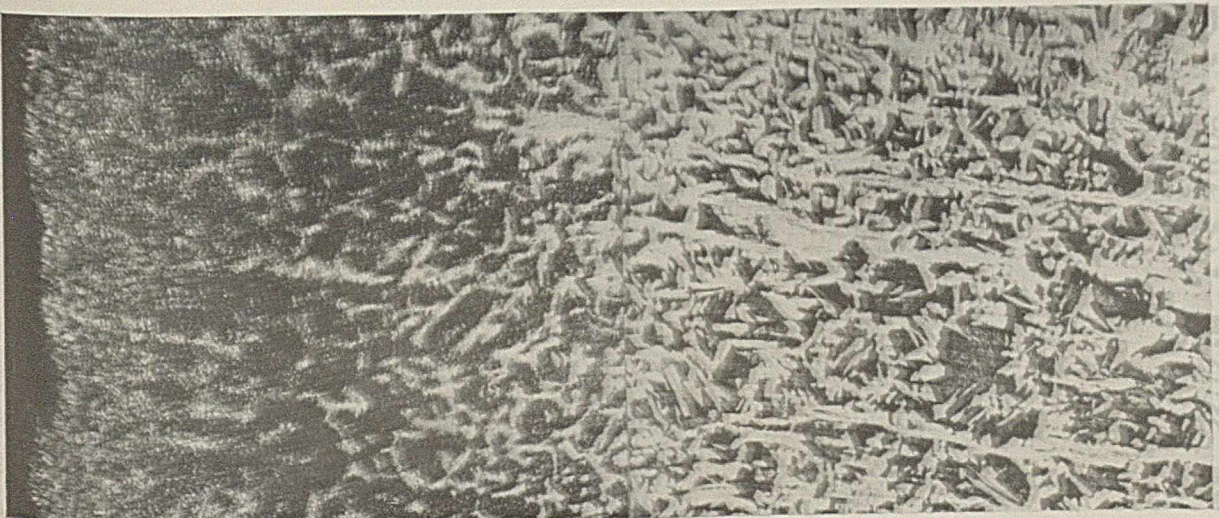


Fig. 32.

to minimize the detrimental effect such as accompanies its crystallization in the normal form appearing in gray cast iron.

In Fig. 20 is shown a photograph to illustrate the utility of the microscope in studying the make-up of materials outside the field of the metals and alloys proper. It is a microsection of a non-metallic base impregnated with a molten metallic compound. The value of the material and its future development depended largely on the nature of the interaction during impregnation. The result might be a single new compound, or two new compounds, or simple solution, or mere mechanical mixture. Chemical analysis proved of little service in this differentiation. But the structure is heterogeneous—this eliminates the single compound or the solid solution. Further microscopic study with selective methods of attack served to identify the constituents and class the product as one of mere mechanical impregnation.

In no field does the microscope become such a useful auxiliary as in the examination of the special or alloy steels; here its usefulness is rather of the future than of the past. It is impossible to dwell upon this phase which is beyond the scope of a paper of this character. It is of interest to note, however, the most important revelation that, in spite of the multiplicity of alloying elements and their various combinations, their influence is largely one of degree and that, after all, the underlying structural considerations are common to all.

While the greatest amount of work of a more scientific nature has been done in the anatomical or structure-composition division perhaps the greatest utility of the microscope in the works laboratory is in the biological division, or that branch correlating the structure changes with the treatment received, for the properties of metals are most vitally dependent upon their mechanical working (whether cast, forged, or rolled) and the heat treatment. Microscopic study, together with determinations with the pyrometer, have given us a rational understanding of the annealing and the tempering of steels. We recognize that the hardening of steels by quenching is due to structural influences occasioned by changes of the relations of carbon and iron; and we can apply this knowledge to advantage in the heat treatment, whereby we can manipulate the properties as desired by taking advantage of the ability to check the structure at any stage between the abnormal one of the quenched state and the normal one of the annealed steel.

One point is vital in this connection and may almost be taken as an axiom. The strength of a steel is inversely proportional to the grain size, and the growth of grain is a result of temperature and time.

Figs. 21-26 are microsections of a steel casting of 0.50 per cent. carbon, and serve to illustrate the marked variations of structure, with consequent changes of physical properties, resulting from heat treatment or mechanical working. Fig. 21 is the steel as cast, with its rather coarse grain due to normal cooling from the high casting temperature. Fig. 22

is the same material after forging, and shows the mechanical breaking down of the grain with a resultant increase of strength. But an annealing of the forged piece at the high temperature of 1100°C . has again (Fig. 23) coarsened the grain, nullifying the effects of forging and leaving the material in no better physical condition than the original casting. A moderate temperature of 800°C ., however, restores the fine-grained structure (Fig. 24). Fig. 25 shows the steel heated to 1000°C . and quenched in water, and gives the typical martensitic structure of a hardened steel. Finally, reheating the material of Fig. 25 to 650°C ., and again quenching, results in the sorbitic texture (Fig. 26), where the transition from the martensitic structure of the hardened steel to the pearlitic structure of the slowly cooled state has been practically completed, but without chance for segregation of the constituents as would be the case if slow annealing had been resorted to. This last figure shows the finest texture it is possible to obtain in steels, and it results, consequently, in the highest combined strength and ductility.

The considerations treated above are of great importance in the control of the annealing and tempering of steels, and have a bearing on the proper finishing temperatures in rolling and forging operations.

In Fig. 27 we have the well-known Roberts-Austen circle, illustrating the marked variations of structure resulting from different heat treatments of a piece of blister steel of 1.50 per cent. carbon, the original structure of which is given in the center.

Fig. 28 is a section of a steel axle broken by fatigue, or continued repetition of stress. The larger grained structure is of the material at fracture, and the fine grain is the result of judicious annealing of the same material. Whether or not the coarse crystallization is the result of the repetition of stress is problematical. It is likely that the original structure in the area of fracture was coarse, favoring therefore the early failure by fatigue because of the more uniform orientation of the crystal cleavages, whereas a fining of the grain by judicious treatment would have resulted in longer life because of a breaking-up of the regularity of cleavage directions.

Figs. 29 and 30 are photomicrographs of a steel rail, the former of the original material, with very good grain, and the latter after heating to high temperature. Remembering our axiom regarding the correlation of grain size and strength, it is evident that the heating has resulted in a marked deterioration in quality. These illustrations point out the reasons for the wearing down at the joints of cast welded track, or the weakness of electric welded rail or any welds made without subsequent treatment. The material shown is not burnt, and the structure of Fig. 30 can be changed to one of good quality by proper treatment, either by judicious annealing or, as is the common practice in welding, by hammering or mechanical working of the material.

Fig. 31 illustrates the effect of punching a piece of structural steel. The distortion produced can be traced back from the edge of the hole by the curvature

of the black pearlitic areas in the direction in which the punch was driven through the plate. The depth of distortion depends upon the thickness of the plate and the size (also the sharpness) of the punch; it can easily be measured, and it has been found that for a three-fourth inch hole in a three-quarter inch plate, about one-tenth inch increase of diameter of hole by reaming is necessary to remove all affected material.

Fig. 32 is a section of a steel casting cut by the oxyhydrogen blowpipe. Passing inward from the cut edge, we note the burnt or oxidized portion in the burnt part immediately adjacent; next the enlarged grain of the overheated but not burnt area; then through a graduation of grain size to the normal structure of the interior. This method seems at first sight to have a very detrimental effect, but is in reality slight, since measurement shows a depth of affected material of only four- or five-hundredths of an inch.

Numerous other instances might be cited of the usefulness of the microscope. It has materially assisted in the determination of the nature of the various zinc coatings for the protection of iron surfaces, and we are trying it out in the study of the progression of rusting on metal specimens.

But it will be necessary to conclude with a comment on the probabilities of the future. While the great field of application of metallographic study has naturally been to the metals and alloys, there is every reason to expect extension of its scope to allied lines, such as the examination of complex ores and slags, to ceramic materials and perhaps to coal and coke. In all of these instances we find good and poor materials of identical analysis; the probability is that the interrelations of the constituents are different. An interesting application along this line has just been pointed out in the use of microscopic examination to detect iron blast-furnace slags which are suitable, or otherwise, as a raw material for Portland cement. That vitrification which is essential in the proper slags is brought out very neatly.

Finally we may look to improvement in the microscope itself. We are at present restricted to the study of the heterogeneous structure revealed by ordinary reflected light. The petrographer has the advantage of being able to use transparent sections and polarized light, and in consequence can determine the crystal systems of the constituents of the rock under examination. When suitable apparatus is perfected (it is now being developed) to enable us to determine the crystal forms of the constituents of an opaque specimen by reflected light, then the metallographic microscope will have a materially enlarged scope of application and utility.

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THE SIZING OF PAPER WITH ROSIN COMPOUNDS.

By J. STEWART REMINGTON, DOUGLAS A. BOWACK AND PERCY DAVIDSON.

Received April 10, 1911.

The sizing of paper, from the standpoint of the chemist, is a problem which is not uncommonly sup-

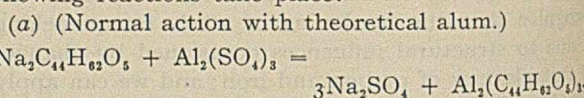
posed to be well understood and fully inquired into, but the true state of the matter is that there is as yet insufficient data available of a nature to determine definitely the actual agencies which perform the function of sizing paper, in confirmation of which he it said that the question has but to be raised to at once introduce a variety of argument and diverse opinions.

Since the publication of Dr. Wurster's treatise on rosin-alum sizing in 1878, our knowledge of chemistry, relating to paper-making, has largely increased, and it is the object of the authors of the present paper to endeavor to summarize the present position of the science, by setting out the results of recent exhaustive researches, in company with a complete criticism of data thereby accumulated, more particularly in connection with the various points concerning rosin sizing, which have long occupied the attention of paper-makers, and paper mill chemists generally.

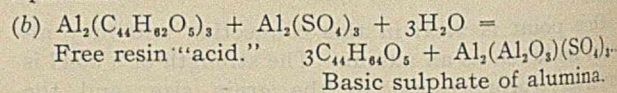
In turning to consider the present time work and views of leading chemists dealing with the science of paper-making, the question which presents itself at the outset is the selection of a fitting subject-material, but it is obvious that in a treatise of this description the essential contents will imply so much of chemistry as is indispensable for the practical investigation, particular stress being laid upon the coöperation of the practical and theoretical issues, which in the past have remained more or less independent one of the other.

In viewing a scheme of this character it becomes clear that in the theoretical treatment of the chemical processes, which in many ways constitutes the most important part of the problem, the chief considerations are: firstly, the composition and properties of the actual sizing agents (*i. e.*, the products of interaction between rosin size and alum and auxiliary precipitants); secondly, their relationship to cellulose itself.

The present generally accepted theory of sizing action assumes that on the addition of alum the following reactions take place:



Since, however, the quantity used in the mill is much greater than this proportion, the excess is supposed to decompose the neutral resinate of alumina with liberation of the free acid, according to the following equation:



To proceed, Dr. Würster, from the results of his original experimental work, took exception to the then current view (which it may be remarked has till now remained unsettled) that the actual sizing agent is a resinate of alumina, formed as above represented, and asserted that the free rosin acids were the active sizing agents. He drew his conclusions from the results he obtained by extracting rosin-sized

paper with ether and other solvents, the residue, after evaporation, being almost entirely composed of free rosin acids. He also found the alumina in the paper before and after extraction to be the same in amount.

Again, as recently as February, 1907, in *The World's Paper Trade Review*, Mr. Edward F. Moody made the following statement in an article on the same subject—"the free rosin being absolutely insoluble in water is a much better sizing agent than the precipitated and more or less soluble alumine resinate." From a large number of experiments we have found that alumina resinate is very slightly soluble in water at ordinary working temperatures. Mr. Moody further states that "there is no doubt that a pound of free rosin is as effective as two pounds of alumina resinate." Our results do not coincide with this.

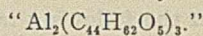
Thus we rapidly reach a fundamental stage in the principles of sizing with rosin soaps. To take the simplest case, What is the best form in which rosin can be applied? One school teaches us that the free rosin is the most valuable constituent of the size—in other words, the more free rosin the size contains, the better the results obtained, upon which theory the custom has developed of making sizes very rich in free rosin, sometimes in the form of an emulsion, containing an exceedingly high percentage of finely divided free rosin particles. On the other hand, some well-known experts maintain that the alum precipitates the size from its solution, producing a complex mixture consisting of alumina resinate and free rosin emulsion. Again, the use of a considerable excess of alum—often more than four times the necessary quantity—is usually recommended. Beyond this important stage, except for the suggestion that the requisite excess has been determined rather by experience than by theoretical calculations based upon scientific grounds, nothing more appears to be known.

Having duly considered the various aspects of this extremely important inquiry, we next approach the details of our work and conclusions on the subject. Any attempt to investigate this problem by experiments conducted on finished sized paper alone is to endeavor to do, at least at this early stage, what is almost impossible. Consequently, we have divided the work of this investigation into three entirely distinct sections, *viz.*: a the theory of the constitution and general properties of the active sizing agents; (b) their reactions under the influence of varying conditions in the beating engines, more especially with regard to their ultimate sizing efficiency; (c) the behavior of cellulose towards such substances, with observations on the deviations from simple additive relations. In the first place, therefore, we will consider the question of the composition and activity of alumina resinate.

In order to isolate the resinates of alumina, the neutral brown size is dissolved in luke-warm water, diluted to a convenient bulk, and the molecular proportion of pure alum, previously dissolved in water, is gradually added to the solution. The compound resinates of alumina, which soon separate, are collected

and rapidly washed with water, until the washings no longer contain salts of sulphuric acid.

The air-dried substance has the approximate composition (mean result of twenty-five determinations),



1.000 grams of anhydrous alumina resinate gave 0.0456 gram alumina, Al_2O_3 .

$$\text{Al}_2\text{O}_3 = 4.56 \text{ per cent.}$$

The aluminum derivative of abietic acid, $\text{Al}_2(\text{C}_{44}\text{H}_{62}\text{O}_5)_3$, requires $\text{Al}_2\text{O}_3 = 4.94$ per cent.

It will be seen from the above results, that the figure for the equivalent of alumina in aluminum resinate is rather lower than that which theory requires for aluminum abietate. Although as a general statement " Al_2H_3 " holds good for aluminum resinate, it must be borne in mind that commercial rosin itself is a mixture of rosin acids and certain other substances, which are not present in constant proportions and have been found on experiment to possess equivalents varying in a greater degree than that which has hitherto been supposed. Consequently, the composition of the mixture of aluminum resinates produced during the reaction with alum and neutral rosin differs with the type of size used.

The anhydrous compound aluminum resinate consists of an amorphous powder: it is of a light buff color, resembling rosin, but usually much softer. It dissolves very readily in cold benzene and chloroform, and it is also readily soluble in hot acetic anhydride, but it is only moderately and sometimes partially soluble in oil of turpentine, petroleum, ether, acetone, ether and alcohol. The solvent effects of the two latter bodies we have dealt with fully, later.

The alumina resinate melts at $135\text{--}140^\circ\text{C.}$, and yields on ignition a mineral ash consisting of alumina, only traces of foreign bases being present.

We propose to show in the following discussion that the absence of alumina in the "ether-extract" of a rosin-sized paper is not direct evidence in support of the claims brought forward by the exponents of the "free-rosin acid" sizing theory. According to Würster's well-known treatise, to which reference has already been made, it is the free rosin acids which are the effective sizing agents. Würster's observations with regard to the extraction and composition of the size obtained from paper with various solvents are perfectly true, and have been repeatedly confirmed during the course of this investigation. The conclusions arrived at, however, are not at all in accordance with the outcome of our present and more expanded inquiry. As far as Würster's experimental determinations go, the conclusions arrived at are natural and in order, but a new factor must now be taken into consideration, which is—that both ether and alcohol readily cause the decomposition of alumina resinates to take place, even in the bone-dry condition, the solvents removing some of the products of dissociation formed during the rearrangement of radicals, which occurs during what is known as sizing. Moreover, it is to be remembered that in practice the free rosin already contained in the size used will naturally

be found in the contents of the preliminary ethereal extract.

The results of some experimental determinations concerning the action of solvents on anhydrous alumina resinate are given in the following table:

TABLE I.

	Ether.		Alcohol.	
	Per cent. of alumina, Al_2O_3 , in residue.	Per cent. of alumina, Al_2O_3 , in extract.	Per cent. of alumina, Al_2O_3 , in residue.	Per cent. of alumina, Al_2O_3 , in extract.
1.....	6.01	1.38	5.40	1.71
2.....	6.51	1.28	6.92	1.52
3.....	6.78	1.25	6.40	1.68
4.....	7.40	1.33	8.72	1.41
5.....	6.66	1.30	6.62	1.51

Alumina resinate was shaken up in the cold with excess of ether and allowed to stand for about half an hour. The filtrate was then decanted off and the residue dried. The filtrate was in turn evaporated to dryness and both extract substances analyzed for alumina.

The above preliminary tests led to the quantitative investigation of the amounts in which the two extracts are present, with the results given below:

TABLE II.

Exp.	Percentage of residue.	Percentage of extract.	Percentage of ash in filtrate extract.	
			Percentage of Al_2O_3 in residue.	Percentage of ash in filtrate extract.
1.....	40.10	59.90	10.40	1.20
2.....	39.40	60.60	9.05	0.67
3.....	33.50	66.50	8.41	1.30
4.....	40.00	60.00	7.41	1.01
5.....	34.15	65.85	6.16	1.27
6.....	37.10	62.90	9.22	1.10
7.....	37.35	62.65	8.30	1.41
8.....	30.00	70.00	9.16	1.06
9.....	33.3	66.70	10.64	0.30
10.....	32.00	68.00	8.80	1.10
11.....	30.50	69.50	9.53	1.02
12.....	35.10	64.90	9.02	0.86

In dealing with the question of the reaction which really does take place between alums and rosin size, it cannot be denied that much confusion is liable to arise, inasmuch as it is a matter of great significance, and of an intricate and complicated nature, such as is rarely encountered in technical investigation. It has been found during the course of the present investigation, that contrary to the general belief, practically no free rosin acids are liberated during interaction with both neutral and excess of alum; that is, provided that there are no active foreign bodies present, such as other metallic salts, and more especially free acid. The last named is an essential consideration, seeing that many technical difficulties, for instance the discoloration and the deterioration of the strength of paper, can primarily be traced to the unfavorable conditions under which it was sized. Up to this point we have assumed that all the alumina molecules attaching themselves to resin acids are held in the ratio of alumina resinate. It is equally conceivable, however, that two units of affinity are united with the resin acids in some cases, and that the alumina resinate may not only be formulated on the basis of the simplest attachment, but that, in others, where a higher alumina equivalent in proportion to the resin acids, is contained a firmer union of these acids with

basic alumina is involved. From the results of a large number of experiments conducted on the precipitation of alumina resinate with neutral alum, and also of excess of alum in various proportions, and further, the influence of acids and alkalis, salts and other alums in these same reactions we have invariably found that aluminum resinate exists in more than one form or condition, and also in conjunction with cellulose itself: hence the observations which we have advanced above, concerning these precipitated mixtures. Reference has already been made to the condition of the anhydrous alumina resinate which remains when the substance dissolved in ether or alcohol is separated. It is evident that some of the sodium resinate contained in neutral size are too weak to react with equivalent dilute solutions of alum, but certain unstable compounds are formed in the presence of the slightest excess of this precipitant. It is in the capacity of these two kinds of substances for uniting to form an active homogeneous compound, or rather, the opportune and consequent effective transformation of the sodium resinate present into certain modifications of resinous compounds, that the real secret of the efficient and perfect sizing of paper lies.

When anhydrous alumina resinate is treated with cold ether (the same applies in a lesser degree to alcohol) for a considerable time, or even extracted in the ordinary way in a Soxhlet separator for about half an hour, it appears to have undergone an unusual process (possibly pre-existent) of dissociation which may be regarded as caused by an uncertain distribution in the first place of the aluminum base between the various resin acids present, especially since the total quantity of the latter is greater than that required for neutralization (see Table II). As regards the properties of the residual compound (aluminum resinate) X: the substance is a hard amorphous body. It has no definite melting point, but shrinks and darkens at a temperature above $300^{\circ}C$. This derivative does not give the (Liebermann-Storch) reaction, acetic anhydride H_2SO_4 , nor is it attacked by any of the usual solvents. Further, it is but little affected by mineral acids. Hot chloroform, however, has the peculiar property of causing this new compound to take the form of a characteristic jelly-like substance.

It seems plain that all available evidence points to the necessity of recognizing the important part played by aluminum resinate during the process of sizing paper. With a view to further justifying a new position, in advocating the value of aluminum resinate as the real sizing agent, the influence on paper of all the existing sizing materials used in connection with engine-sizing have been investigated, and the results obtained are in complete harmony with those previously arrived at.

Before turning to the data derived from the various paper trials some explanation must be forthcoming to account for the behavior of solvents during the estimation of rosin in paper by the ordinary methods. It has long been known that ether alone does not extract all the resin from paper, and the course invariably recommended is to acidulate the ether with

either acetic or hydrochloric acid, in order to permit of complete extraction. It has also been noted by many observers that the partially extracted paper is not altogether absorbent; in other words, not entirely desized. The experimental data collected and summarized in the following table goes to show that the free rosin in paper is not the most important sizing agent. The sample papers used for this research were manufactured from specially prepared stock, with a view to distinguishing between the added rosin and resinous bodies pre-existing in the pulp furnish of the paper. Moreover, the papers were sized with known quantities of certain market brands of rosin soaps.

TABLE III.—TABLE OF EXTRACTS. SOLVENT ETHER.

Exp.	Description of papers (all unloaded).	Time. Hrs.	Preliminary rosin extract.	Further extract after decomposition.	Acid used.	Total extracted rosin.	Percentage of ether extract under neutral conditions.
1	Imitation parchment	3	1.66	0.47	HCl	2.13	77.93
2	"	3	1.96	0.36	Acetic	2.32	84.40
3	"	3	1.86	0.35	"	2.21	84.10
4	"	3	1.77	0.41	"	2.18	81.20
5	"	3½	1.87	0.22	"	2.09	90.00
6	"	4	1.85	0.23	HCl	2.08	88.90
7	Manila insulating	3	1.92	0.27	Acetic	2.19	89.60
8	"	3	1.89	0.28	HCl	2.17	87.10
9	Brown wrapper sized	5	0.22	0.08	"	0.30	73.30
10	"	3½	0.21	0.08	Acetic	0.29	72.40
11	"	7	0.18	0.07	"	0.27	66.60
12	"	4	0.20	0.09	"	0.29	69.00
13	"	3	0.22	0.09	"	0.31	72.90
14	"	2	0.19	0.04	HCl	0.23	82.60
15	"	3	0.20	0.10	"	0.30	66.60

In all cases the papers extracted according to the column showing results with ether alone were only partially desized and still ink-resisting. Furthermore, according to the existing methods of analysis, a certain proportion of the remaining alumina resinate, though their functions are destroyed, are left behind.

It has been shown in the preceding sections, on the basis of many experimental results, that alumina resinate exists in more than one form and much information has been collected towards the solution of these sizing problems from the behavior of the alumina resinate in the nascent state. A careful consideration of the facts pointed out in the following discussion will show that these influences may be regarded from two different standpoints, *viz.*, that of the stable form alumina resinate, and that involving the formation of still more complicated compounds.

The freshly precipitated or hydrated neutral resinate of alumina is readily soluble to a clear solution in the usual solvents. On continued digestion with ether and alcohol, an extremely interesting and important reaction takes place. In the cold, no essential change is noticeable but, on warming, a white flocculent precipitate gradually settles out, which substance, on analysis, is found to be identical in composition with the residue previously obtained by extraction of the anhydrous alumina resinate, already described. It contains a higher molecular proportion of alumina, and the resinous components appear to have under-

gone a change. The substance itself possesses entirely different physical and chemical properties from those of the normal alumina resinate, which at once confirms our previous impression, that either a process of condensation has taken place, or that the molecular relations of the alumina and rosin acids have been submitted to a rearrangement. The fact that the change is accompanied by a kind of dissociation of the resin acids is very significant, and is the opening of an entirely new field of research, on and around the constitution of resin acids.

To resume: we believe that the explanation of many of the vagaries of sizing lies here, and the essential sequence is, therefore, to make plain, by means of data derived from practical experiments and observations, the full effect of sizing agents under all known conditions. The details of the sizing of trial sheets are given in the following table, in condensed form, in order to render results convenient for the purposes of comparison.

NOTES AND OBSERVATIONS.

The trials are numbered approximately in the order of importance which they occupy in this scheme of classification. The majority of the papers of this series were made from bleached sulphite and soda pulp, and subjected, as nearly as possible, to similar treatment in the beaters. "Neutral size" (column 2) refers to a solution of sodium resinate, containing no free rosin, while the term "ordinary size" indicates that a stock size, containing about 6-8 per cent. of free rosin, was used.

An explanation of the signs employed in the preceding table are herewith given:

(\odot) = Extra free beater pulp.

(\otimes) = Extra wet pulp.

The following is a brief summary of the chief deductions made from the results of this investigation.

It is obvious that in making a relative comparison of the respective merits of the two sizing agents which have in the past been considered of primary importance, the part played by "free rosin" can lay no claim to any particular scientific value. The most general conclusion to be drawn is that nascent alumina resinate already fulfils the essential conditions of a true size, and that, both theoretically and practically speaking, the neutral resinate is a highly effective sizing agent. In actual practice the reaction is in accordance with the general rule above stated, the excess of alum required being only slight, in order to counteract the hardness of the water, and any large excess unnecessary. Further, the excess alum has no effect whatever upon the alumina resinate first formed, and the idea that alumina is precipitated by the soda of the rosin soap, when reaction with alum takes place, has nothing to recommend it. It is true that papers made from moderately wet beater stuff possess a natural resistance to water, and when sized with free rosin in sufficiently large quantity they become hard-sized, solely by virtue of a mechanical surface action on the basis of the fact that the heat of the drying cylinders serves to melt together the small particles

TABLE IV.—PAPER TRIALS.

Exp. No.	Material used.		Precipitant.	Quantity.	Size precipitant.	Sizing agent.	Ink-resisting properties.		Effect of the various chemicals on the paper. Remarks, etc.
	Pulp.	Size.					How sized trade terms.	Standard test seconds, ¹	
1	Unbleached soda	Neutral size	Alum	3%	Chemical equivalent	Alumina resinate	Very hard	410	
2	"	"	"	4 1/2%	"	"	"	450	Excellent surface
3	Bleached soda ²	"	"	5%	"	"	Extra hard	Over 1000	"
4	"	"	"	5%	"	"	Hard	205	
5	Unbleached sulphite ¹	"	"	3%	"	"	Medium	45	
6	"	"	"	5%	"	"	"	55	
7	Bleached soda	"	"	5%	Slight excess	"	Hard	200	
8	Unbleached sulphite	"	"	5%	"	"	Medium to hard	120	Loaded with kaolin
9	"	"	"	6%	"	"	Hard	220	Excellent surface
10	"	"	"	3%	Large excess	"	Medium	35	
11	" ¹	"	"	5%	"	"	"	45	
12	"	Ordinary size	"	3%	Chemical equivalent	Alumina resin and free rosin	"	30	
13	Unbleached sulphite	"	"	5%	Slight excess	Alumina resinate and free rosin	Hard	110	Good surface
14	"	"	"	12%	Large excess	"	"	165	Sizing properties are not entirely relative to quantity
15	"	Neutral	Aluminum hydrate	3%	Chemical equivalent	**	Not sized	2	
16	"	"	"	5%	"	**	"	2	
17	"	"	"	5%	Excess	**	"	3	
18	"	"	Nil	3%	Nil	**	"	1	
19	"	Ordinary size	"	6%	"	**	"	4	
20	"	Neutral	Sulphuric acid	3%	3%	Free rosin	"	2	Causes weakening of the pulp
21	"	Ordinary size	"	6%	6%	"	"	7	Brittle and speckled
22	"	Nil	"	Nil	6%	**	Slightly	10	Parchmentized and brittle
23	"	"	"	"	Large excess	**	Not sized	4	General rotting effect
24	Unbleached sulphite	Nil	Alum	"	10%	**	"	2	Hardened
25	"	"	"	"	20%	**	"	3	Hardened
26	"	"	Caustic soda	"	10%	**	"	1	Softened
27	"	Free rosin	Nil	3%	Nil	**	"	4	
28	"	"	"	5%	"	**	"	4	
29	"	"	"	8%	"	**	"	5	Speckled
30	"	Soln. of free rosin in alcohol	"	4%	"	*	"	1	
31	"	"	"	12%	"	Free rosin	Slightly	10	Heavily speckled
32	"	Free rosin	Alum	3%	3%	"	Not sized	5	
33	"	Rosin in alcohol	"	6%	10%	Free rosin	Slightly	15	Speckled
34	"	"	"	12 1/2%	15%	"	Hard	100	Varnished, unevenly sized, and brittle
35	"	"	Sulphuric acid	6%	3%	"	Not sized	5	Speckled
36	"	"	"	12 1/2%	3%	"	Hard	180	Varnished, unevenly sized, and brittle
37	Unbleached sulphite	Free rosin	"	5%	3%	**	Not sized	1	
38	"	Nil	Aluminum hydrate	Nil	4%	**	"	1	
39	"	Free rosin	"	3%	Chemical equivalent one-half	**	"	1	
40	"	"	"	5%	1%	**	"	1	
41	"	Nil	Nil	Nil	Nil	**	"	1	
42	"	"	Froth oil	"	"	**	"	1	
43	Unbleached soda	"	Nil	"	"	**	"	1	
44	"	"	Froth oil	"	"	**	"	1	
45	"	Free rosin	Nil	3%	"	**	"	1	
46	"	"	"	5%	"	**	"	3	Speckled
47	Unbleached sulphite	Alumina resinate (anhydr.) ¹	"	3%	"	**	"	2	
48	"	Alumina resinate (hydrated) ¹	"	5%	"	**	"	3	
49	Unbleached sulphite	Alkaline soln. of alumina resinate	Nil	5%	Nil	**	Not sized	1	Softened
50	"	Alumina resinate (anhydr.) ¹	Alum	5%	3%	Alumina resinate	Slightly	7	Hardened

¹ The aluminum resinate was applied under ordinary conditions. The papers were run off on a model Fourdiner machine, all being of equal thickness, but not glazed or calendered.

of free rosin, forming what may be best described as a varnish, continuously, though unevenly distributed. Moreover, it has been repeatedly stated by a number of observers that free rosin particles are the effective "sizing agents:" consequently, it occurred to us to try the effect of dispensing with the double operation as carried out in our modern beating engines, and going one step further, to use an all free-rosin emulsion in place of the usual high free-rosin sizes. The results of many attempts, however, were unsatisfactory and conclusive.

Under ordinary circumstances, using normal quantities of size, rich in or entirely composed of free rosin, however intimately the free rosin may have penetrated into the fiber, it will not hard-size it.

The conclusions which have been arrived at by the sizing tests on a practical scale, and also those based upon entirely different considerations, *i. e.*, the behavior of alumina resinate itself, seem to be in striking opposition to much of the doctrine hitherto formulated, and we are brought now to the question of the part played by cellulose in the order of reactions in relation to sizing. Now, Messrs. Cross and Bevan (see work 1900, etc.) suggest that cellulose would decompose the neutral resinate by combining with alumina, and also simultaneously with the rosin acids. From this, one may presume that compounds of "cellulose-alumina resinate" may possibly exist, which would conveniently explain away some of the previous difficulties. Experimental work goes to prove to us that, although such compounds undoubtedly exist, they are only formed under certain circumstances, or, one might say, special conditions, which, under the existing "modus operandi" of paper mills, are liable to be overlooked. As a general statement, it is admitted that when the condition of the pulp in the beater is basic the alumina resinate is partially broken up, and the cellulose, when in the right state, displays a strong affinity towards it, the evolved compound becoming more active by virtue of the union of the cellulose with the resinates of alumina. This subject we propose to treat with in detail in a later publication. It is worthy of note that this type of reaction cannot be said to be constant for all varieties of cellulose, as it has been frequently observed that the completeness of the interactions vary considerably with different kinds and conditions of cellulose. The study of the compound celluloses (so far as this investigation has taken us) regarding their reactions with alumina resinate has led to their division into two classes. For example, according to the previous "conditioning" one can obtain two very dissimilar sizing effects on the same pulp, though using exactly the same proportions of size. In one, predominating, the distinctive properties of alumina resinate may be easily recognized. In the other mixture, many of the properties of the chief components are changed, which can beyond all doubt be affirmed to be due to the formation of a new chemical compound. We are thus disposed to consider the distinction between the various mixtures and chemical compounds, produced during the course of engine-sizing, as being only relative to the primary condition of the cellulose.

In conclusion, it can be anticipated from the foregoing remarks that the hope of a speedy and definite settlement of this question will be justified when the chemical changes which take place between cellulose and alumina resinate are more widely known and that the importance of righting these doubtful issues will be recognized.

AYNSOME TECHNICAL LABORATORIES,
LANCASHIRE, ENGLAND.
March 29, 1911.

THE CHEMISTRY OF ANAESTHETICS, II: EXAMINATION OF COMMERCIAL OXYGEN.¹

By CHARLES BASKERVILLE AND RESTON STEVENSON.

A critical study of the many chemicals used for anaesthetic purposes and the modern methods of administration involves the use of oxygen. This paper records the results of the examination of commercial "C. P." oxygen of the various kinds procurable on the market, for its strength and medicinal and chemical purity.

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A. BIBLIOGRAPHY.

1. *The Methods of Preparation of Oxygen.*

The alchemists² were probably acquainted with oxygen, perhaps also the Greeks³ in the fourth century, and the Chinese,⁴ long before Priestley's experiments. In 1630, Jean Rey⁵ knew that certain metals, when heated, fix a portion of the air, and in 1674 Mayow prepared oxygen from niter. In 1771, Scheele⁷ prepared a gas by heating several oxides, including the black oxide of manganese, and, at about the same time, Cavendish⁸ studied oxygen. To Priestley,⁹ however, has been given the honor of discovering oxygen as a constituent of the air. Davy¹⁰ and Lavoisier¹¹ later studied the preparation and nature of this gas.

¹ Read at the regular March meeting of the New York Section of the American Chemical Society, 1911.

² Bolton, *Am. Chem.*, **4**, 170.

³ Hoefler, *Histoire de la Chimie*, **2**, 271.

⁴ Duckwood, *Chem. News*, **53**, 250.

⁵ Jean Rey, *Essai sur la recherche de la cause pour laquelle l'estain et le plomb augmentent de poids quand on les calcine*. Bazas, 1630.

⁶ Mayow, Rodwell, *Chem. News*, **8**, 113.

⁷ Scheele, *Chemische Abhandlung von der Luft und dem Feuer*. Upsala u. Leipzig, 1777.

⁸ Cavendish, *Trans. Roy. Soc.*, **56**, 432; **74**, 119, 170; **75**, 372.

⁹ Priestley, *Ibid.*, **62**, 147; **65**, 384; **73**, 398; **75**, 279; **78**, 147, 313; **79**, 7, 289; *Experiments and Observations on Different Kinds of Air*, London, **2**, 29 (1775-1777); **3**, 1; *Experiments and Observations Relating to Various Branches of Natural Philosophy*, London, **1**, 192 (1779).

¹⁰ *Trans. Roy. Soc.*, **101**, 1.

¹¹ *Chem. J. (Crell)*, **4**, 440; **5**, 125; *Chem. Ann. (Crell)*, **1**, 33, 136 (1786); **1**, 354, 441, 528, 550, 552 (1788); **2**, 55, 262, 431, 433 (1788); **1**, 145, 162, 260, 323 (1789); **2**, 68, 145, 433 (1789); **1**, 69, 518 (1790); **1**, 71 (1791); **1**, 29 (1803).

At the present time, there are the following methods of preparation and manufacture of oxygen:

1. *Heating of Chlorates.*—In 1785, Berthelot prepared oxygen by heating potassium chlorate, and, after him, many investigators¹ have studied the reaction upon heating chlorates and perchlorates. Pure oxygen was made by Stas² by heating potassium chlorate and perchlorate, with or without silica, and several investigators³ have devised apparatus for the generation of the gas by heating chlorates.

2. *Heating Chlorates with Various Substances.*—Döbereiner showed that CuO, etc., lowered the temperature of decomposition of KClO₃, and Gay-Lussac and von Humboldt used moistened KClO₃, and showed that the presence of MnO₂ aided the decomposition. Subsequent investigators⁴ have studied the catalytic action of the oxides of all the metals and of such substances as CdSO₄, platinum black, metals, etc. Others⁵ have patented apparatus for generating oxygen by these processes.

3. *From Hypochlorites.*—Dingler, in 1829, made the observation that bleaching-powder, when heated with the oxide of nickel, cobalt, or copper, evolved oxygen, and Mitscherlich, in 1843, made oxygen by decomposing bleaching-powder. Subsequently it was prepared by heating hypochlorites with MnO₂,⁶ with Fe₂O₃,⁷ with platinum black in sunlight,⁸ with BaO₂,⁹ and with CaO,¹⁰ by heating a solution of hypochlorite with substances such as cobalt peroxide¹¹ and H₂O₂Aq;¹² and Jaubert has devised apparatus and prepared oxygen by the reaction with water of pastilles of bleaching-powder mixed with Na₂O₂,¹³ or with the sulphates of nickel, copper, and cobalt.¹⁴

4. *Reaction of Chlorine and Water.*—D. Müller¹⁵ showed that water vapor and chlorine at 120° form O₂ + HCl. Others¹⁶ have studied this reaction and made modifications in the process.

5. *Heating Sulphuric Acid or Sulphates.*—De Luca¹⁷ made oxygen by passing H₂SO₄ over pieces of porcelain in a hot tube; and Deville and Debray,¹⁸ by heating ZnSO₄ and by squirting H₂SO₄ upon red-hot leaves

of platinum or upon pieces of brick; and Archerau,¹ by heating a mixture of sand and gypsum. Archerau studied also the effects of various metallic oxides upon the decomposition of H₂SO₄ to form oxygen.

6. *Heating Various Solid Substances and Mixtures.*—Priestley prepared oxygen from KNO₃ and from MnO₂; Scheele, from HNO₃; Deville, from NaNO₂ and from Ba(NO₃)₂; Webster,² from NaNO₃ + ZnO; Guertler,³ from CuB₂O₇ at 1000°; and Hilpert⁴ obtained slowly a 5 per cent. reduction of Fe₂O₃ at 1350°. Various apparatus⁵ for the generation of oxygen by heat have been devised.

7. *Combustion of Solid Mixtures.*—These mixtures generate oxygen by burning after they are kindled and consist of a chlorate with combustible matter,⁶ of a chlorate and substances such as iron and zinc oxalate;⁷ or of alkali peroxides mixed with hydrated salts.⁸

8. *Reaction of Peroxides with Water and Aqueous Solutions.*—The following reactions may be used as a source of oxygen: MnO₂ or BaO₂ or PbO₂ with acids;⁹ permanganates or dichromates with acids;¹⁰ H₂O₂ + KMnO₄;¹¹ H₂O₂ + K₂Fe(CN)₆;¹² H₂O₂ + ammoniacal CuSO₄ and other catalytic agents;¹³ water + K₂(CO₃), and other "per" salts or salts with H₂O₂ of crystallization;¹⁴ and water + alkali peroxides with which have been incorporated various substances to retard or accelerate reactions or to improve the keeping quality.¹⁵

9. *Electrolysis.*—The production of oxygen in acid and alkaline solutions with iron, lead, etc., electrodes of various shapes, with or without diaphragms, has been studied by many investigators.¹⁶ Hydrogen,

¹ Archerau, *Chem. Centr.*, **36**, 999 (1865).

² J. H. Pepper, *Chem. News*, **6**, 218 (1862); D. Campbell, *Ibid.*, **6**, 268 (1862); Anonymous, *Ibid.*, **6**, 287, 299, 310 (1862).

³ *Z. anorg. Chem.*, **38**, 456 (1904).

⁴ *Ber.*, **42**, 4893 (1909).

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⁶ Cie. Française de l'Acétylène Dissous, French Pat., 332,098, 1903; Jaubert, French Pat., 350,377, 1904; Jaubert, French Pat., 361,322, 1905; Jaubert, French Pat., 361,537, 1905; Jaubert, Eng. Pat., 22,034, 1909.

⁷ C. Zeiss, Eng. Pat., 17,809, 1910; Turner, *Am. Chem. J.*, **37**, 106 (1907).

⁸ Böck u. Wanz, German Pat., 218,257, 1908.

⁹ Scheele, *Chem. Ann.* (Crell), **2**, 229, 291 (1785); J. Robbins, *Chem. News*, **9**, 126 (1864); Boettger, *J. prakt. Chem.*, **107**, 48; Tonneau, *Union Pharm.*, **45**, 304 (1893); Tommasi, *Chem.-Ztg.*, **17**.

¹⁰ Balmain, *Ann.*, **44**, 217 (1842); Guyard, *Mon. Sci.*, Aug., 1882; Riggs, *J. Am. Chem. Soc.*, **1903**, 876.

¹¹ Voracek, *J. pharm. chim.*, **6** (1882); Lindner, *Chem.-Ztg.*, **9**, 776 (1885); Gohring, *Chem.-Ztg.*, **12**, 1659 (1888); Seyewitz and Poizot, *Compt. rend.*, **144**, 86 (1907); Mosler, *Chem.-Ztg.*, **1909**, 785.

¹² Kassner, *Chem.-Ztg.*, **13**, 1302, 1338, 1407.

¹³ Vitali, *L'Orosi*, **1895**, 1.

¹⁴ *Pharm. Zentr.*, **45**, 705 (1904); E. Merck, German Pat., 213,457, 1907; P. Dame, French Pat., 390,520, 1907.

¹⁵ Robbins, *Chem. News*, **9**, 126 (1864); Jaubert, *Compt. rend.*, **134**, 778; Jaubert, French Pat., 340,388, 1904; Foersterling and Phillip, U. S. Pat., 788,256, 1905; Ageron, French Pat., 352,452, 1905; Roessler and Hasslacher Chem. Co., French Pat., 366,524, 1906; Roessler and Hasslacher Chem. Co., French Pat., 366,326, 1906; Walter, *Chem.-Ztg.*, **32**, 1066 (1908); Sarason, Eng. Pat., 23,676, 1908; Sarason, French Pat., 405,644, 1907.

¹⁶ Garuti, Eng. Pat., 15,588, 1882; Latchinoff, Eng. Pat., 15,935, 1888; Habermann, *Z. angew. Chem.*, **1892**, 323; Swinburne, *Inst. of Elec. Eng.*, July, 1892; Garuti and Pompili, Eng. Pat., 23,663, 1896; Hammerschmidt und Hess, *Chem.-Ztg.*, **22**, 123; A. Coehn, Eng. Pat., 23,478, 1893; Crepy, *La Rev. Techn.*, July, **1898**, 292; Schoop, *Z. Electrotechn.*, **18**, 241 (1900); Schoop, *Sci. Abstracts*, [1] **4**, 76 (1900); Bell, Eng. Pat., 78,146; Siemens and

¹ Buchholz, *J. für Chem.* (Schweigger), **6**, 219 (1817); *Pharmacopée Française*, **1837**; *Pharm. Centr.*, **8**, 591 (1837); Jungfleisch, *Bull. soc. chim.*, **15**, 6 (1871).

² Stas, *Chem. News*, **73**, 15.

³ Toecke, *Ber.*, **17**, 1831 (1885); Sweetzer, Eng. Pat., 12,245, June, 1895; Mangianeli, French Pat., 409,962, March, 1909.

⁴ Lenard, *Compt. rend.*, **41**, 341 (1855); Krebs, *Chem. Centr.*, **41**, 305 (1870); Jungfleisch, *Bull. soc. chim.*, Aug. 4, 1871; Bandrimont, *J. Chem. Soc.*, **24**, 1151 (1871); Bandrimont, *Mon. Sci.*, Nos. 357 and 358, 1872; Stas, *Chem. News*, **73**, 15 (1873); Loewe, *J. Chem. Soc.*, **27**, 1056 (1874); Wiederhold, *Pogg. Ann.*, **116**, 171; **118**, 186.

⁵ Fowler and Grant, *Chem. News*, **61**, 117; Brown and Stedman, Eng. Pat., 21,067, Oct., 1898; Blackie, Eng. Pat., 9,772, April, 1898.

⁶ Keller, *Rep. für Pharm.* (Buchner), **1848**, 48.

⁷ Artlet, *Chem. News*, **12**, 159 (1865).

⁸ Schönbein, *J. prakt. Chem.*, **98**, 76 (1866).

⁹ Zinno, *Les Mondes*, **1877**.

¹⁰ Beltzer, U. S. Pat., 968,528, 1910.

¹¹ Fleitmann, *Chem. News*, **11**, 255 (1865); Bidet, *Bull. soc. chim.*, **45**, 81 (1886).

¹² Volhard, *Ann.*, **253**, 246 (1890).

¹³ Jaubert, Eng. Pat., 11,466, 1901.

¹⁴ Jaubert, French Pat., 325,627, 1902; French Pat., 333,603, 1903.

¹⁵ *Compt. rend.*, **40**, 906 (1855).

¹⁶ Binks, *Chem. News*, **8**, 168 (1863); Teller, *J. Soc. Chem. Ind.*, **1890**, 246; Charlopin, U. S. Pat., 713,602, 1902.

¹⁷ De Luca, *Compt. rend.*, **53**, 156 (1860).

¹⁸ Deville and Debray, *Compt. rend.*, **1860**.

ozone, moisture and carbon dioxide are the usual impurities.

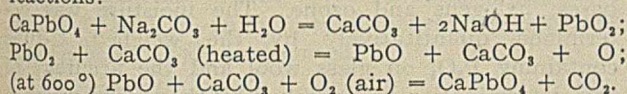
10. *From the Air by Means of Mercury.*—Lavoisier obtained oxygen from the air by formation of HgO by boiling mercury and then decomposing this red oxide by heat.

11. *From the Air by Means of Cu_2Cl_2 .*—Mallet¹ found that by passing air over Cu_2Cl_2 with moist sand above 100°, Cu_2OCl_2 was formed; and at 400°, oxygen is evolved and Cu_2Cl_2 reformed.

12. *From the Air, by Means of BaO_2 .*—Upon heating BaO_2 , oxygen is evolved and at a lower temperature the oxygen is taken from a stream of air to reform the BaO_2 . Boussingault² and, after him, many others³ have studied this process, devising apparatus and determining the most advantageous conditions of temperature, of pressure, and of the physical structure of the peroxide. Others⁴ have tried the effect of incorporating MgO, CdO, CuO, etc., with the BaO_2 .

13. *From the Air, by Means of Manganates.*—Tessie du Montay⁵ and, subsequently, many others⁶ have studied the production of oxygen by decomposing red hot Na_2MnO_4 by steam and then regenerating it by a current of air at a higher temperature. Various forms of apparatus have been devised and the best conditions of temperature, of pressure, and of the physical structure of the manganate have been determined; and various substances,⁷ such as kaolin, CuO, Na_2SO_4 , NaOH, and MnO_2 , have been incorporated with the manganate to give it a proper physical condition and catalytic activity. Ozonizing⁸ the air has also been tried.

14. *From the Air, by Means of Plumbates.*—Kassner⁹ obtained oxygen from the air by the following reactions:



Obach, Eng. Pat., 11,973; Garuti and Pompili, Eng. Pat., 27,249, 1903; Richards and Landis, *Trans. Am. Electrochem. Soc.*, **3**, 105 (1903); Richards and Landis, *Ibid.*, **4**, 111 (1904); Oerlikon Co., *Electrochem. Met. Ind.*, 1904, 293; Varelle, French Pat., 355,652, 1905; L. von Scoyar, U. S. Pat., 813,844, 1906; Cowper-Cowles, Eng. Pat., 14,285, 1907; Eycken, Leroy, Moritz, French Pat., 397,319, 1908; Coehn and Osoka, *Z. anorg. Chem.*, **34**, 86 (1903).

¹ Mallet, *Compt. rend.*, **64**, 226 (1867); **66**, 349; J. Phillips, *J. Chem. Soc.*, **24**, 859 (1871).

² Boussingault, *Ann. chim. phys.*, [3] **35**, 5; *Compt. rend.*, **32**, 261, 821 (1851); *J. Chem. Soc.*, **5**, 269 (1852).

³ G. and A. Brin, Eng. Pat., 157; G. and A. Brin, Eng. Pat., 1,416, 1880; Gondols, *J. del'Eclairage du Gaz.*, **1870**, 453; Thorne, *J. Soc. Chem. Ind.*, **8**, 82; Ellice-Plack and Chappman, Eng. Pat., 16,987, 1887; Ellice-Plack and Chappman, Eng. Pat., 1,844 and 3,880, 1888; A. Brin, Eng. Pat., 3,967, 1888; Brin's Oxygen Co., and Murray, Eng. Pat., 14,918, 1893; Price, Eng. Pat., 14,213, 1903; G. von Ach, U. S. Pat., 944,473, 1909.

⁴ Wanklyn, *Polyt. J.*, **213**, 2641 (1872); Gondola, *Compt. rend.*, **66**, 488.

⁵ Tessie du Montay and Marechal, Eng. Pat., 85, 1866; *Chem. News*, **14**, 154 (1866); *Bull. soc. chim.*, **1866**, 398; Tessie du Montay, *Polyt. J.*, **196**, 230 (1868).

⁶ "American Artisan," *Chem. News*, **20**, 44 (1869); Fenta, Eng. Pat., 10,667, 1891; Parkinson, Eng. Pat., 9,457, 1891; Fenta, Eng. Pat., 3,034, 1891; Fanta, *J. Soc. Chem. Ind.*, **11**, 312 (1892); Chappman, Eng. Pat., 19,078, 1892; Lapointe, Eng. Pat., 13,959, 1895; Dutremblay and Lugan, *J. pharm. chim.*, **6**, 392 (1897); Felt, Eng. Pat., 21,299, 1898; Felt, U. S. Pat., 702,855, 1908.

⁷ Bowman, Eng. Pat., 7,851, 1890; Parkinson, Eng. Pat., 14,925, 1890; Webb and Raynor, Eng. Pat., 13,036, 1891; Chappman, Eng. Pat., 11,504, 1892; Hitchcock, *Eng. Min. J.*, **3**, 67 (1899); **4**, 11, 83.

⁸ Lawson, Eng. Pat., 15,998, 1890.

⁹ Eng. Pat., 11,899, 1889.

Plumbates of barium and strontium also were used. Kassner's process was modified¹ to use CO_2 from flue gases, instead of Na_2CO_3 ; and other investigators² have determined the best apparatus and conditions for the process.

15. *From the Air, by Means of Dialysis.*—Graham³ proposed the separation of oxygen by its greater rate of diffusion through colloid septa and through capillaries. Further study⁴ has been made in the effort to adapt this process to commercial use.

16. *From the Air, by Means of Absorption.*—In various substances, such as charcoal, water, alcohol, turpentine, glycerine, naphtha, ether, acetone, chloroform, salt solutions, etc., oxygen is more soluble than nitrogen and can in that way be separated from the air.⁵ Investigators of this process for different solvents and various conditions of temperature, pressure and concentration, indicate that it cannot be applied industrially.

17. *From the Air, by Means of Living Matter.*—Oxygen has been prepared by the natural and artificial respiration of plants,⁶ but not upon an industrial scale. The absorption in blood⁷ has also been studied.

18. *From the Air, by Means of Condensation and Distillation.*—Linde prepared oxygen by the fractional distillation of liquid air. Subsequently, modifications⁸ have been suggested by many investigators, in order to effect a better heat interchange in the distillation and condensation; to use the temperature and energy of expansion and the matter of the residue rich in nitrogen; to employ fractional condensation as well as fractional distillation; and to perfect the mechanical arrangements.

II. Methods of Analysis of Oxygen.

1. *Qualitative Tests.*—The presence of oxygen is shown by these changes: Blue CrCl_2 to green CrCl_3 ; white indigo to blue; colorless NO to brown NO_2 ; darkening of alkaline pyrogallol; white Fe(OH)_2 to blue Fe(OH)_3 , slightly oxidized; blue Fe(OH)_2 ,

¹ Reitz, *J. Soc., Chem. Ind.*, **1890**, 104, 120; **1891**, 71.

² *J. Soc. Chem. Ind.*, **9**, 187 (1890); Langsdon, Eng. Pat., 6,553, 1890; *J. Soc. Chem. Ind.*, **10**, 380 (1891); Kassner, *Polyt. J.*, **204**, 136 (1891); **278**, 468; Kassner, *J. Soc. Chem. Ind.*, **1889**, 885; **1890**, 187; Kassner, *J. Gasbel.*, **34**, 351 (1891); Kassner, *Chem.-Ztg.*, **17**, 1242 (1894); *Compt. rend.*, **117**, 109 (1894); Timm, Eng. Pat., 10,632, 1901.

³ Graham, *J. Chem. Soc.*, **20**, 235 (1867).

⁴ Margis, French Pat., 17,981, 1881; D'Argand, *Bleiblatler*, [1] **31**, 44 (1879); Herzog, *Chem. News*, **59**, 99; Neane, Eng. Pat., 6,463, 1890; Villepigne, Fournier, and Shenston, Eng. Pat., 19,044, 1896.

⁵ Angus Smith, *Proc. Roy. Soc.*, **12**, 424; Montmagon and de Laire, *Jahresber.*, **1868**, 922; Montmagon and de Laire, *Polyt. J.*, **193**, 434; Mallet, Eng. Pat., 2,137, 1867; Deville and Debray, *Compt. rend.*, **87**, 441 (1878); Helouis, *Ber.*, **1882**, 1221; Reynolds, *J. Soc. Chem. Ind.*, **1890**, 246; G. Claude, *Compt. rend.*, **131**, 447; Bilbie and Wanklyn, Eng. Pat., 8,923, 1899; Brünler, French Pat., 391,213, 1908; Descours-Desacres, French Pat., 396,889, 1908; Levy, Eng. Pat., 5,931, 1909.

⁶ Dutrochet, *Compt. rend.*, **3**, 499 (1836); Schultz, *Ibid.*, **19**, 524 (1844); Boussingault, *Ibid.*, **19**, 945 (1844); Berzelius, *Jahresber.*, **1848**, 267; Boussingault, *Compt. rend.*, **53**, 862 (1862); Böhm, *Biedermann's Centr.*, **1878**, 12.

⁷ Montmagon and de Laire, *Jahresber.*, **1868**, 922.

⁸ Linde, German Pat., 88,824; Schröter, *Engineer*, **1895**, 325; Hampson, Eng. Pat., 7,559, 1896; Thrupp, Eng. Pat., 18,913, 1900; H. A. Strong, Eng. Pat., 9,142, 1900; Le Seuer, Eng. Pat., 4,828, 1901; Pictet, *Engineering*, **1901**, 368; Linde, *Z. Ver. Ing.*, **46**, 1173 (1902); G. Claude, French Pat., 322,702, 1902; G. Claude, *Compt. rend.*, **137**, 783 (1903); Pictet, French Pat., 322,600, 1900; Soc. pour l'exploitation des Procédés, G. Claude, French Pat., 328,245, 1903; Levy and Helbronner, French Pat., 328,770, 1903

to brownish yellow¹ $\text{Fe}(\text{OH})_3$; turning brown of a solution of NaMnO_4 .² Christomanos³ recommends an ethereal extract of a mixture of $\text{Cu}(\text{NO}_3)_2$ solution + PBr_3 , the ether extract turning green, and the lower layer purple-red.

2. *Determination by Phosphorus.*—Oxygen is accurately determined by the slow combustion of phosphorus.⁴ It has been recommended that⁵ a solution of phosphorus in castor oil, etc., be used, electrically heating the solution for gas mixtures rich in oxygen. Pure oxygen is not absorbed by phosphorus, the absorption beginning at 565 mm. partial pressure and is violent; a gas containing more than 50 per cent. oxygen should not be analyzed by this method.

3. *Determination by Alkaline Pyrogallate.*—Pyrogallol with an excess of KOH absorbs oxygen at all partial pressures readily and accurately.⁶ Its accuracy has been questioned⁷ because of the formation of CO , but this can be prevented by the proper choice of conditions,⁸ particularly by a large excess of KOH .

4. *Determination by Various Methods.*—Priestley's reaction of oxygen with NO was found accurate by some observers⁹ and inaccurate by others.¹⁰

The absorption by freshly precipitated $\text{Fe}(\text{OH})_2$ ¹¹ was considered untrustworthy by Liebig.¹² De Koninck¹³ recommends absorption by an alkaline solution of ferrous tartrate, and Linossier⁴ used this solution with phenosafranine as an indicator.

A solution of Na_2SO_3 ¹⁵ absorbs oxygen and this solution may be titrated by means of ammoniacal cupric sulphate. Mohr¹⁶ questioned the accuracy of this method.

Oxygen is absorbed by solution of $\text{CrCl}_2 + \text{HCl}$,¹⁷ but Berthelot¹⁸ maintains that this solution evolves some hydrogen.

A copper spiral heated electrically,¹⁹ or in any other way, absorbs oxygen, and at room temperature, oxygen

J. E. Johnson, Jr., U. S. Pat., 783,045, 1905; J. E. Johnson, Jr., U. S. Pat. 933,462, 1905; R. Merves, French Pat., 360,427, 1905; R. Merves, French Pat., 358,236, 1905; Hazard-Flamand, Eng. Pat., 26,720, 1908; Hazard-Flamand, Eng. Pat., 27,592, 1908; Soc. L'Air Liquide, French Pat., 410,967, 1909; Pictet, French Pat., 409,787, 1909; F. Schmidt, French Pat., 403,630, 1909; Janecke, French Pat., 407,852, 1909; Le Seuer, *Met. Chem. Eng.*, 8, 234 (1910); Röttger, French Pat., 413,958, 1910.

¹ Fuchs, *Am. J. Sci.*, 16, 397 (1829); cf. Thoms, *Ber. Pharm. Ges.*, 1894, 240.

² Phillips, *Am. Chem. J.*, 16, 340.

³ *Verh. Ges. Deut. Naturf. Aerzte*, 1905, II, 76.

⁴ Boussingault, *Compt. rend.*, 58, 777 (1864); Otto Lindemann, *Z. anal. Chem.*, 18, 158 (1879).

⁵ Centreiszwer, *Chem.-Ztg.*, 34, 494 (1910).

⁶ Liebig, *Ann.*, 77, 107 (1850).

⁷ Calvert, *Compt. rend.*, 57, 873 (1863); Cloez, *Compt. rend.*, 57, 875 (1863); Boussingault, *Compt. rend.*, 57, 885 (1863).

⁸ Weyl and Goth, *Ber.*, 14, 2659 (1882); Clowes, *Chem. News*, 74, 199 (1896); *Hempel's Gas Anal.*, Dennis, 1906, 149.

⁹ Wanklyn, *Chem. News*, 62, 263 (1890); 65, 49 (1892); Kreider, *Z. anorg. Chem.*, 13, 418 (1896).

¹⁰ De Koninck, *Z. angew. Chem.*, 1891, 78.

¹¹ Hart, *Z. anal. Chem.*, 1869, 482; Mohr, *Ibid.*, 12, 138 (1874).

¹² *J. Chem. Soc.*, 26, 935 (1873).

¹³ *Z. angew. Chem.*, 1890, 727.

¹⁴ *J. pharm. chim.*, [5] 23, 103 (1891).

¹⁵ Schutzenberger and Géroordin, *Compt. rend.*, 75, 879 (1873); Schutzenberger and Risler, *Bull. soc. chim.*, [2] 19, 152 (1873); Graham, *Mem. Chem. Soc.*, 3, 46.

¹⁶ *Z. anal. Chem.*, 12, 138 (1874).

¹⁷ Von der Pfordten, *Ann.*, 225, 112.

¹⁸ Berthelot, *Compt. rend.*, 127, 24.

¹⁹ F. Fischer, *Ber.*, 12, 1696; Von Jolly, *Ann. physik*, N. F., 6, 520.

is absorbed by copper¹ with a solution of $(\text{NH}_4)_2\text{CO}_3$, to absorb the CuO which is formed and thus to keep the surface of the copper clean.

Also proposed for the determination of oxygen, is this process:² the gas is mixed in a flask with a solution of MnCl_2 , and then $\text{KI} + \text{NaOH}$ are added; the Mn_2O_4 settles out and HCl is added in excess, and the iodine which is evolved is titrated.

B. THE ANALYSIS OF COMMERCIAL OXYGEN.

I. The Methods of Analysis Used.

The following sorts of matter may be suspected to exist in a cylinder of oxygen gas:

1. Solids. 2. Liquids. 3. Gases and vapors: H_2O ; halogen acids, HNO_3 , organic acids; O_3 , NO_2 , N_2O , SO_2 ; NH_3 , organic bases; CO_2 , halogens, oxides of chlorine; HCN , $(\text{CN})_2$; PH_3 , SbH_3 , AsH_3 , H_2S ; H_2 ; CO , CH_4 , organic matter; N_2 , N_2O , rare gases of the atmosphere.

For these impurities, a qualitative search was first made and then, whenever necessary, a quantitative determination. The following systematic procedure was used:

Experiment (a).

Train:

Cylinder; Trap + red and blue litmus paper and starch-KI paper; P_2O_5 , U-tubes (1) and (2); CaCl_2 tube; moistener + red and blue litmus paper and starch-KI paper; $\text{Ba}(\text{OH})_2$ solution (1); NaOH solution; AgNO_3 solution; 2 CaCl_2 tubes; CuO furnace; CaCl_2 , U-tubes (1) and (2); $\text{Ba}(\text{OH})_2$ solution (2); NaOH tube; gasometer.

By this experiment any solids and liquids were caught in the trap, and the litmus and starch-potassium iodide papers would show the presence of acids, bases, halogens and ozone. The moisture was determined quantitatively by the weighed U-tube containing P_2O_5 on glass wool and the accuracy of this determination was checked by the second weighed P_2O_5 U-tube. The CaCl_2 tube protected the P_2O_5

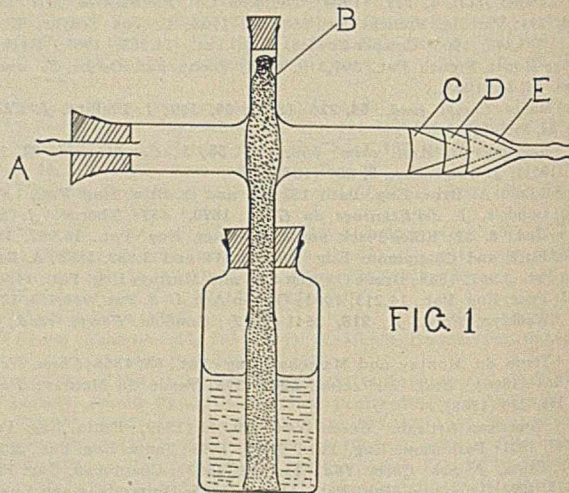


FIG. 1

U-tube from absorption of water from the moistener. This apparatus is shown in Fig. 1. The gas enters at A; it then passes the wet porous cotton rope B,

¹ Hempel, *Z. anal. Chem.*, 20, 499 (1881).

² Winkler, *Ibid.*, 28, 366 (1889); Chloropin, *Chem. Centr.*, 1899, i, 372.

which does not contain enough water to absorb the impurities from the gas but does moisten it enough to enable the impurities in it to react with test papers; and then the gas passes through cones *C*, *D* and *E* of litmus and starch-potassium iodide papers, repeating with moistened gas the tests made before in the trap tube. The nearly saturated $\text{Ba}(\text{OH})_2$ solution showed the presence or absence of CO_2 , and after the run, this solution was divided into three portions: the first portion was acidified with HCl and tested for SO_3 ; the second portion with $\text{HNO}_3 + \text{AgNO}_3$, for halogens and halogen acids and oxides of chlorine; and the third portion was set aside. After the run, the NaOH solution (2 : 3) was divided into three portions: to the first portion was added BaCl_2 , and then HCl in excess, thus testing for CO_2 , SO_2 , SO_3 ; the second portion was acidified with HNO_3 , then made ammoniacal, AgNO_3 was added and then the solution was made acid with HNO_3 , thus testing for SO_2 , H_2S , halogens, halogen acids and chlorine oxides; the third portion was mixed with the third portion of the $\text{Ba}(\text{OH})_2$ solution (see above) and tested for HCN and $(\text{CN})_2$ by boiling with $\text{Fe}(\text{OH})_2 + \text{Fe}(\text{OH})_3$ and acidifying with HCl to form Prussian blue.

The AgNO_3 solution repeats some of the previous tests and in addition shows the absence or presence of PH_3 , SbH_3 , and AsH_3 . The gas is then dried by the two CaCl_2 tubes, and the H_2 and organic compounds are oxidized by the red hot CuO . The water which is formed is weighed in the CaCl_2 U-tube (1), which is guarded by the weighed CaCl_2 U-tube (2); and the CO , which is formed is absorbed in the nearly saturated $\text{Ba}(\text{OH})_2$ solution (2). This last tube is guarded by a tube containing solid NaOH . The gas is measured in the gasometer. From 10 to 18 liters of gas were usually passed in from 3 to 6 hours; the separate bubbles could easily be counted.

Experiment (b).

Train:

Cylinder; trap and litmus paper and starch-KI paper; starch-KI solution; FeSO_4 solution, slightly acid; KMnO_4 solution; gasometer.

The trap and test papers used in experiment (a) were again used in this experiment, so that the tests were repeated in an accumulative manner. The starch-KI solution gives a test for ozone, and portions of this solution were tested before and after the run with methyl-orange and phenolphthalein to indicate acids and bases in the gas. The slightly acid solution of FeSO_4 is titrated before and after the passage of the gas to show the presence of active oxidizing agents. Naturally, it would appear that the oxygen gas would itself oxidize this solution, but such is not the case.¹

The KMnO_4 solution, made by adding one drop of $\text{N}/2$ KMnO_4 to 500 cc. of water, tests for reducing agents.

By these two experiments, qualitative tests are made for all likely constituents of the gas, except the following:

¹ The stability of FeSO_4 in solution in the presence of oxygen and air at various temperatures, etc., has been investigated by the authors, *J. Am. Chem. Soc.*, **33**, 1104.

Oxygen, which is determined quantitatively; N_2 and the rare atmospheric gases, which are obtained by difference; and N_2O , for which no sensitive test is known. It is assumed to be absent. Further tests for CO^1 were found unnecessary, since no organic matter was detected, except in one sample, and, in that instance, only a faint trace.

In addition to the quantitative determinations of H_2O and H_2 made in experiments (a) and (b), determinations of CO_2 and O_2 were made as follows:

Experiment (c).

CO_2 was determined by absorption in a NaOH solution (2 : 3) saturated with O_2 , and weighing.

Experiment (d).

The sample of gas was measured over water in an Elliot apparatus consisting of a 100 cc. burette surrounded by an air jacket, CO_2 and oxygen were absorbed by fresh alkaline permanganate, and the gas residue was measured over water in a tube of small bore.

The alkaline pyrogallol was made up according to Hempel,² 5 grams pyrogallol in 15 cc. $\text{H}_2\text{O} + 120$ grams KOH in 80 cc. H_2O . These solutions were mixed and immediately poured into "individual" bottles, each containing just more than enough for analysis. The KOH (c. p. "by alcohol") used for this solution was fused and about 1/20th of its weight of Na_2O_2 added; the temperature of the mixture was raised until oxygen was liberated in abundance and then cooled somewhat; the melt was poured into water which caused the evolution of more oxygen and the solution boiled free of gas. It then contained no alcohol or other organic impurities. Determinations of the CO in several gas residues showed that about 0.05 per cent. CO is formed in this analysis and this amount was added as a correction to the percentage of oxygen.

II. Results of Analysis.

Below is given a tabulation of the results of analyses, according to the methods given above, of seven makes of commercial "C. P." oxygen. The percentages represent the volumetric proportion of the different constituents of the gas just as it emerged from the cylinder and not upon the dry basis.

ANALYSIS.								
No.	Source of oxygen.	O_2 .	H_2O .	CO_2 .	H_2 .	Organic Matter.	N_2 , etc.	All other impurities
1	$\text{KClO}_3 + \text{MnO}_2$	93.20	0.30	0.11	0	0	6.39	0
2	$\text{KClO}_3 + \text{MnO}_2$	98.31	0.14	present	0	0	1.54	0
3	$\text{KClO}_3 + \text{MnO}_2$	92.82	0.26	trace	0	0	6.92	0
4	$\text{KClO}_3 + \text{MnO}_2$	97.13	0.23	present	0	trace	2.63	0
5	Liquid air	96.10	0.15	0.01	0	0	3.74	0
6	Electrolysis	99.23	0.35	0.03	0.14	0	0.25	0
7	$\text{Na}_2\text{O}_2 + \text{H}_2\text{O}$	99.20	0.50	trace	0	0	0.30	0

III. Conclusions.

The seven samples of oxygen examined by us were all medicinally pure. For some purposes they were ready for use, but for calorimetry, elementary organic analysis by combustion, gas analysis, etc., they would have required previous purification or else a correction for the impurities present.

¹ Hempel, *Gas Analysis*, Dennis, 1906, p. 212.

² Hempel, *loc. cit.*, p. 49.

C. STANDARDS OF PURITY RECOMMENDED FOR OXYGEN TO BE USED IN MEDICINE.

The gas should be neutral toward moist delicate litmus paper; and when passed through an aqueous solution of silver nitrate, it should produce no turbidity. Not more than an opalescence should be produced when 2 liters of the gas are passed slowly through an aqueous solution of barium hydroxide. When 5 liters of the gas are passed slowly through an aqueous solution of sodium hydroxide, then over heated copper oxide, and finally through an aqueous solution of barium hydroxide, no turbidity should be produced. The gas should contain at least 94 per cent. oxygen upon the dry basis. As supplied for use, the gas should contain no liquids and no solids.

COLLEGE OF THE CITY OF NEW YORK,
APRIL, 1911.

THE DETERMINATION OF VANADIUM IN VANADIUM AND CHROME-VANADIUM STEELS.

By J. R. CAIN.

Received May 5, 1911.

INTRODUCTION.

Vanadium has been called by metallurgists a "homeopathic" remedy because of the remarkable results obtained by small additions of it to other metals, notably to steel. Carbon steels or alloy steels as produced in this country, when they carry vanadium, usually contain from 0.10-1.00 per cent. It has been claimed by some that the element acts by removing dissolved gases, especially nitrogen, from the molten steel, with resulting elimination in the slag of the greater part added, and that the amount left in the steel itself is of secondary importance. However, others have shown that the microscopic structure of steel is greatly modified by the residual vanadium in the amounts in question here, and, as might be expected, there are corresponding changes in physical properties. Hence it will be seen that a high degree of accuracy in determining vanadium in steel is to be desired. Considerations such as these, combined with requests from many sources, led the Bureau of Standards to undertake the preparation of a vanadium standard steel similar to the analyzed plain carbon steels which it has issued for some time. In conformity with the usual practice of the Bureau, samples were analyzed by its chemists and by prominent technical and works chemists (eleven in all). The first figures thus obtained for vanadium were so unexpectedly discordant as to indicate sources of error in methods used which had probably been overlooked or unrecognized. Accordingly, some of the most probable of these were investigated by the Bureau. The results of this investigation were communicated to those participating in the coöperative work, and a satisfactory concordance in the final vanadium figures was very soon obtained. Inasmuch as some of these sources of error do not seem to have been sufficiently emphasized in the literature, concise statements regarding them may be of service. Three classes of methods were used by the coöperating analysts:

Class A.—Methods like that first described by Campagne¹ and found with little variation from the original in many text-books on steel analysis. The hydrochloric acid (ferric) solution of the steel is extracted with ether, which removes most of the iron, leaving the vanadium in the aqueous layer. This portion is evaporated to dryness and the operation repeated two or three times with fresh portions of hydrochloric acid. The latter reduces the vanadium to the quadrivalent state; the final evaporation is made with sulphuric acid and is continued until fumes are given off strongly. The solution is then titrated against permanganate.

Class B.—Methods depending upon the reduction of quinquivalent to quadrivalent vanadium by ferrous sulphate, either by titrating directly against a ferrous solution or adding excess of the same and titrating back with bichromate; potassium ferricyanide is used either as an external indicator or by adding it directly to the solution undergoing titration.

Class C.—Most of the iron is extracted as under Class A, the hydrochloric acid replaced by nitric acid and the vanadium separated from iron, chromium, etc., by pouring into a boiling solution of sodium hydroxide. The vanadium goes into the filtrate, and is precipitated by mercurous or lead salts, the final estimation being either gravimetric or volumetric.

It seems likely that these three classes of methods comprise those most used in this country, inasmuch as the group of coöperating chemists was typical. The same methods are used with little or no change for the analysis of chrome-vanadium steels carrying usually from 0.2-5 per cent. chromium.

SOME SOURCES OF ERROR.

General Errors.—An error in all methods where final titration is made against permanganate may arise by failure to deduct the blank caused by the presence of elements other than vanadium; this may be particularly high in such methods as that of Campagne where, if the ether extraction is not carefully done, there may be large amounts of ferric sulphate present during the titration. Campagne himself² speaks of this point, but it is not usually mentioned in text-books. If salts yielding green or blue solutions are present these may obscure the true end-point, requiring several tenths of a cubic centimeter of tenth-normal permanganate in excess. Indeed, in low vanadium products the blank may be much larger than the amount required by the vanadium, or if the analyst does not make a qualitative test for vanadium he may report its presence when the steel contains none. Another point to be observed is the temperature of the solution being titrated. The optimum temperature is 70-80° C.³ It is almost impossible to secure a good end-point in a cold solution. On the other hand the work of Sarkar and Dutta⁴ and of others on the reduction of permanganate by hot sulphuric acid

¹ *Ber.*, **36**, 3164 (1903).

² *Loc. cit.*

³ Hillebrand, "Analysis of Silicate and Carbonate Rocks," *Bull.* **423**, p. 151, U. S. Geol. Survey.

⁴ *Z. anorg. Chem.*, **67**, 225 (1910).

solutions of manganous sulphate shows the importance of not titrating at too high a temperature.

Errors Incident to Methods of Class A.—(1) During the ether extraction there is almost always some iron reduced to the ferrous condition; this is not always reoxidized during the course of the analysis before the titration and therefore might be calculated as vanadium if this fact is not taken into consideration.

(2) The ether, or impurities in it, may act on the strong sulphuric acid when the solution is evaporated to small volume with this acid. There are then present substances which may act on permanganate. In this laboratory separation of carbonaceous material has been observed at this stage, with accompanying odor of sulphur dioxide.

(3) The addition of sulphuric acid before the solution has been repeatedly evaporated with fresh portions of hydrochloric acid is to be avoided, because, if the sulphuric acid is added before reduction of vanadium to the quadrivalent state has been attained, the reduction is likely to be incomplete.

(4) If the evaporation with strong sulphuric acid is too prolonged or carried out at too high a temperature the reverse reaction, resulting in the oxidation of vanadium tetroxide to vanadium pentoxide by the sulphur trioxide, may take place.¹

(5) No other metals capable of oxidation to higher valence by permanganate should be present. Those most likely to be encountered in steel analysis are chromium, molybdenum, and tungsten. The latter two may be removed before titration without great difficulty; the methods hitherto given for separating vanadium and chromium are so laborious that this precaution is often omitted in the case of chromium. A correction for the latter is invariably necessary, particularly in some steels where the chromium and vanadium may be present in the ratio of twenty or forty to one. Moreover, the amount of chromium oxidized to chromic acid is greater when titration is made at 70–80°, as is imperative for a good vanadium end-point, than where the solution is titrated cold, as is sometimes recommended. For details regarding this correction for chromium see "Analysis of Silicate and Carbonate Rocks."²

Errors Incident to Methods of Class B.—Methods requiring the use of ferricyanide as indicator for ferrous salts, when quadrivalent vanadium and ferrous salts are also present, must of necessity be very uncertain, yet these are the conditions under which the determination is carried out. The reason for this is very evident when it is remembered that ferricyanide in acid solution rapidly oxidizes quadrivalent vanadium to the quinquevalent condition with resulting production of ferrocyanide. The latter reacts at once with the ferric iron, so that a blue color is present in the drops of indicator as soon as an appreciable amount of vanadium is reduced and long before the color due to excess of the titrating solution makes its appearance. Consequently such methods, if at all applicable, must yield results varying with the operator and requiring

arbitrary and uncertain correction factors. Much difficulty was experienced in attempting to determine vanadium in pure vanadium solutions by this method; the reason for this, as stated above, was soon discovered, and later, references to the same matter were found in the literature.¹

Errors Incident to Methods of Class C.—Vanadium is almost always carried down by the precipitate of ferric and chromic hydroxides, etc., upon pouring into sodium hydroxide. Usually two or three precipitations are necessary to obtain all the vanadium in the alkaline filtrate. The difficulty seems to be largely due to the presence of manganese, which of course the ether does not extract, for by working in the absence of manganese it has been found possible to make good separations with one precipitation. However, there is no simple method for removing manganese at this stage of a vanadium determination in steel without introducing other complications. If chromium is present another difficulty is added, for part of the manganese is oxidized by the air and precipitated while the sodium hydroxide solution is being boiled to secure complete precipitation of chromium and complete extraction of vanadium from the precipitated hydroxide; this peroxide rapidly oxidizes some of the chromium to chromate, which goes into the filtrate with the vanadium. If the sodium hydroxide precipitation is repeated, or a third precipitation is necessary, as may happen, a very large amount of chromium goes into the filtrate. In fact, the first operation leaves enough chromium with the vanadium to introduce serious error in determining the latter unless a correction is made; furthermore, the same cause may require appreciable correction to be applied to the chromium. The addition of sulphurous acid to the acid solution of the steel just before it is poured into the alkali, as is recommended sometimes, does not help, for of course it is not effective after the solution is strongly alkaline. Another source of trouble is the organic matter mentioned above as sometimes coming from ether; this causes appreciable amounts of iron and chromium to dissolve in the filtrate with the vanadium. It is evident that all of the sources of difficulty, except the last mentioned, are present in even greater degree when an attempt is made to carry out the caustic soda separation without a preliminary extraction of most of the iron by ether. Thus it will be seen that to separate the vanadium from the iron and to obtain all of it in the filtrate may be, and usually is, a long and complicated operation. When this is accomplished there may be present a large amount of chromium, and this occasions another series of difficulties, for the chromate precipitates with the vanadate, whatever the method of precipitation. The only alternative is to titrate the vanadium in presence of the chromium, making the uncertain corrections above-mentioned, or to make an electrolytic separation as described later.

When attempt is made to extract vanadium from steel by fusion of the oxides obtained by evaporation

¹ Koppel and Behrendt, *Z. anorg. Chem.*, **35**, 156 (1903).

² Hillebrand, *Bull.* **422**, pp. 152-4, U. S. Geol. Survey.

¹ Campagne, *Loc. cit.* Brearley and Ibbotson, "Analysis of Steel Works Materials," p. 89.

and baking a nitric acid solution of the metal, an old method which is now probably little used for this class of material, the same series of difficulties as enumerated under Class C is encountered. It seems almost impracticable to extract quantitatively, say one-tenth of 1 per cent. of vanadium in this manner without undue expenditure of time and labor.

It is clear, then, that there are marked defects in the most commonly used methods for determining vanadium in steel, unless the analysis is conducted with extreme care, requiring more time than is usually available in a technical laboratory, or unless the analyst is so experienced that he can recognize and correct for disturbing factors. Accordingly, the present research was started with the hope that a simpler and more accurate procedure might be outlined, and one which would at the same time be reasonably short.

PRELIMINARY WORK TOWARD A NEW METHOD FOR VANADIUM.

Much work was done with the idea of determining vanadium without a preliminary separation from iron. It seemed possible that the vanadium might be oxidized to vanadate and then reduced by hydrobromic acid by distilling in an apparatus suitable for collecting the liberated bromine in alkali. The difficulty, however, is to secure oxidation of the vanadium and then get rid of the excess of oxidizer without at the same time reducing some vanadic acid. It was found that the vanadium of a dilute sulphuric acid solution of a vanadium or chrome vanadium steel could be oxidized easily enough in the cold by manganese dioxide without converting any noticeable amount of chromium to chromate, the excess of manganese dioxide being eliminated by filtration. But when such a solution was placed in the distilling apparatus and distilled after the addition of a large excess of hydrochloric acid and potassium bromide, as recommended by Edgar,¹ there was almost always more bromine liberated than corresponded to the vanadium present. Many efforts were made to get rid of the disturbance, such as long boiling of the oxidized steel solution before placing in the distilling apparatus, reduction of the amount of sulphuric acid used for solution to the minimum necessary, etc., but while the results were usually as accurate as those obtained by any of the methods above described there were occasional and unexplained irregularities which finally led to the abandonment of the method for technical purposes. This is regrettable, for, theoretically, such a procedure is ideal; practically it would be extremely short and simple. It seems likely that the trouble experienced was due either to the known solubility of manganese dioxide in sulphuric acid or to the action of sulphuric acid itself on the hydrobromic acid in the strongly acidified solution in the distilling flask.

From this it appeared desirable to develop a method which would obtain the vanadium in a solution free from all other metals, so that one might always be certain that the oxidizing or reducing action, which-

ever is made the basis of a volumetric method, is exerted by vanadium compounds and nothing else. The manner of accomplishing this was suggested in part by a dissertation of Albert Steffan² who used barium carbonate for precipitating vanadium and chromium, together with relatively little iron, from the (ferrous) solution of the steel. The principle at the base of the method has long been applied to other separations. It has invariably been recommended until recently to conduct this precipitation in the cold, shaking frequently and allowing to stand for many hours. It has been found, however, by numerous experiments here that a few minutes' boiling with the carbonate will completely precipitate much larger amounts of vanadium and chromium than are likely to be encountered in steel analysis; furthermore, the precipitates are free from manganese, a distinct advantage, from many standpoints over the ether separation. The shortening of the time required for precipitation when solutions are boiled has recently been noted by others in connection with steel analyses; also the use of zinc oxide as a precipitant.³ The precipitate obtained in this way contains the insoluble matter from the solution of the steel, a little iron, all the chromium and vanadium, and a considerable excess of the precipitant. The vanadium and chromium may be extracted by fusion with sodium carbonate, but the barium holds vanadium tenaciously and more than one fusion is usually necessary, so that this way of handling the precipitate, although apparently simpler, is longer than the one to be described later.

Smith³ describes an electrolytic method for separating vanadium from iron by driving the latter into a mercury cathode, and in another section he gives directions for electrolytically precipitating chromium under practically the same conditions, hence it appeared feasible to separate both iron and chromium from vanadium by electrolysis when the three are together. Preliminary experiment showed this to be possible, and it was then decided to dissolve the precipitate mentioned above in appropriate manner and submit it to electrolysis in order to obtain a pure vanadium solution. It seemed desirable, however, to be rid of the excess of the precipitant before electrolyzing. The necessary excess being relatively large, it would take too long to drive the iron and chromium out of solution if the precipitant were to accompany them into solution and be deposited along with them, as would be the case with zinc oxide, for instance. Moreover, it seemed desirable to dissolve the steel in sulphuric acid, as the electrolytic deposition is made from sulphate solution. This of course made inconvenient the use of barium carbonate as precipitant. It was therefore decided to try the suitability of cadmium carbonate for the purpose, with the idea of throwing out the excess of cadmium by hydrogen sulphide from the acid solution of the carbonate precipitate. This method gave entirely satisfactory results; the rate of precipitation of the

¹ "Ueber die Bestimmung von Kleinen Mengen an Chrom und Vanadium in Gesteinen und Stahlarten," Zurich, 1902.

² Slavik, *Chem.-Ztg.*, **34**, 648 (1910).

³ "Electroanalysis," fourth edition, p. 258.

¹ *Am. Jour. Sci.*, **27**, 174 (1909).

vanadium and chromium seems even more rapid than with zinc oxide or barium carbonate. The precipitate of cadmium sulphide obtained in a boiling, very slightly acid solution is easily filtered and never carries down vanadium.

The precipitation of vanadium and chromium from a reduced and boiling solution of steel by any of the precipitants herein mentioned succeeds equally well in hydrochloric or sulphuric solutions, but seems to proceed a little faster with cadmium carbonate and a sulphate solution.

THE METHOD IN DETAIL.

Dissolve 2-4 grams of steel in 40-60 cc. of 10 per cent. (by volume) sulphuric acid, in a covered 300 cc. Erlenmeyer flask. Filter off the insoluble, wash two or three times with water, ignite and fuse for a few minutes with acid potassium sulphate, adding the aqueous solution of the fusion to the main solution. If the steel will not dissolve readily in sulphuric acid, hydrochloric acid may be used, fusing the insoluble as before.¹ Nearly neutralize the solution of the steel with saturated sodium carbonate solution. Then add finely pulverized cadmium carbonate in small portions at intervals of four or five minutes, boiling vigorously between times, keeping the flask well covered. A gram or two of carbonate should remain undissolved at the end of the operation. About fifteen or twenty minutes' boiling always suffices. The time may be even shorter for vanadium steels containing little or no chromium. Allow the precipitate to settle and filter rapidly, so as to prevent oxidation and precipitation of iron on the filter (an 11 cm. S. and S. No. 589 white label filter is recommended). Wash the precipitate twice with hot water; no care need be taken to remove all of it from the flask. Dissolve the precipitate with the minimum of nearly boiling 10 per cent. sulphuric acid, catching the filtrate in the flask. Boil to insure solution of material adhering to the sides of the flask. Cool and nearly neutralize with ammonia; there should be no more free acid present than is necessary to prevent the iron from precipitating by hydrolysis when the solution is boiled. Pass a rapid current of hydrogen sulphide for a few minutes while the solution is boiling vigorously. Let the precipitate settle, filter it off and wash two or three times with hot water. Concentrate the filtrate if necessary and electrolyze in a volume of 60-70 cc., using 5-6 amperes at 6-7 volts. The amount of mercury used in the special apparatus described below was about 200 grams. The solution is tested for iron by ferricyanide; usually when no iron test is obtained all the chromium is removed. However, should there be an unusually large amount of chromium relatively to the iron this might not happen. In this case the test should be made by removing 3 or 4 cc. of the solution, adding a few drops of hydrogen peroxide and boiling for a few minutes after the brown color, due to vanadium peroxide,

¹ In this case the carbonate precipitate must be dissolved in sulphuric acid and the separation repeated in sulphate solution, for the precipitate first obtained contains enough chloride to give trouble if dissolved in sulphuric acid and directly electrolyzed.

disappears. If the solution now remains clear and colorless, on adding ammonia, the electrolysis is ended. Acidify the test portion with sulphuric acid before returning it to the electrolyzing apparatus. The simpler ferricyanide test usually answers for all purposes; the complications mentioned earlier, due to reduction of ferricyanide by quadrivalent vanadium, do not interfere in this case, inasmuch as there is no ferric iron to react with the resulting ferrocyanide. When the solution no longer gives a test for iron or chromium, remove it from the apparatus and wash the mercury two or three times with 25 or 30 cc. of water while the current is still passing. Add 2 or 3 cc. of sulphuric acid (1:1 by volume), heat to 70° or 80° C. and add permanganate from a pipette until there is a strong pink color. Run sulphur dioxide into the boiling solution for a few minutes; then pass a rapid current of carbon dioxide until the escaping steam gives no test for sulphur dioxide. Filter, preferably through asbestos¹ or a Munroe crucible, cool the solution to 70° or 80° C. and titrate against *N*/50 potassium permanganate. For extreme accuracy repetition of the reduction and titration is recommended. The reduction may also be made by hydrogen sulphide, if desired.² With special facilities a determination may be completed in 1½ hours, or less.

NOTES AND PRECAUTIONS.

Sufficient exclusion of air is secured by dissolving the steel in a flask kept well covered by a watch-glass. The fusion of the insoluble is absolutely necessary, as a large proportion of vanadium remains here; indeed, Nicolardot has proposed methods whereby, with complete exclusion of air, it is possible to secure practically all the vanadium in the insoluble portion when operating on certain classes of materials. This makes a quick and easy qualitative test for vanadium in steel, for as soon as the carbon is burned off the characteristic appearance of the fused vanadium pentoxide is very striking.

The treatment of the insoluble requires but a few minutes. The operations of solution, of cadmium precipitation and of filtration, must be done promptly, for a delay between solution and precipitation gives opportunity for oxidation of iron. This is to be avoided since it increases the amount of iron going into the carbonate precipitate, thereby prolonging the electrolysis, and also interfering with the complete precipitation of the vanadium and chromium. In this latter connection it seems that the particles of carbonate become rapidly coated with the excessive precipitate of ferric hydroxide, and this interferes with

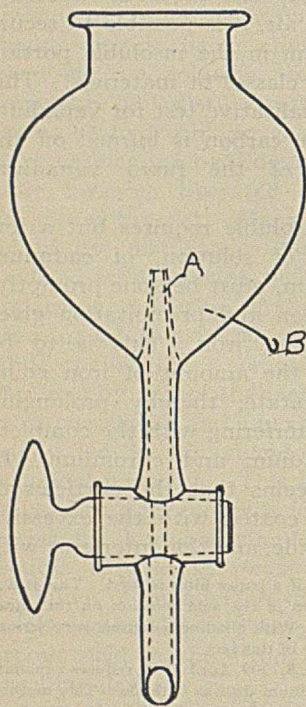
¹ The result will be slightly high if a paper filter is used. This is due to the hydrolyzing and solvent action of the acid solution on the paper (even the best washed filter paper). With alkaline solutions very serious errors may be incurred from ignorance of this fact.

² Bleeker, *Met. and Chem. Eng.*, 9, 209, April, 1911, reduces vanadate solutions electrolytically, using a platinum dish as cathode. This method appears short and simple and might be adopted in many cases. No work has been done here, however, along this line and the exact conditions for complete reduction to the hypovanadate stage, and no further, would probably have to be determined. It is not safe to titrate directly the solution obtained by electrolyzing as described without the preliminary permanganate oxidation followed by reduction and filtration as above; to do so usually gives irregular results.

their efficiency in neutralizing the solution. The operations of filtering and washing must be particularly rapid; there is no difficulty here if the solution, after boiling, is allowed to stand a few minutes before filtering; the precipitate settles readily and is easily filtered. Two washings with hot water are sufficient. Sometimes a little difficulty is experienced in dissolving the precipitate completely from the filter; this is particularly true if the filtration and washing have not been done rapidly and promptly, giving opportunity for a difficultly soluble coating to form over the surface, due to oxidation and precipitation of iron. However, this trouble will never be serious if the operations are conducted as directed; moreover, even if this iron is not all removed from the filter it is never found to contain vanadium after two or three washings with the dilute acid. The advantage of a carbonate precipitant over an oxide precipitant is shown here, because the carbon dioxide evolved during the process of solution very effectually breaks up the difficultly soluble surface layer, permitting the acid to get at the main body of the precipitate. On the other hand, when using zinc oxide it is often very difficult to dissolve the precipitate with dilute sulphuric acid. The hydrogen sulphide precipitation of the excess of cadmium is accomplished quickly; the solution should be nearly neutralized with ammonia; sodium hydroxide or carbonate should not be used, as in this case sodium would be driven into the mercury during electrolysis, not only prolonging this operation, but introducing other complications; if the degree of acidity is right and a rapid current of

hydrogen sulphide is used, the solution being boiled vigorously while this is passing, the cadmium sulphide settles readily and is easy to filter and wash. The solution after filtration can be transferred at once to the electrolytic apparatus which may have any of the usual forms, such as the convenient small beakers with sealed-in platinum wires at the bottom, described by Smith.¹ If many determinations have to be made, however, the apparatus shown in the figure has been found very convenient.

The apparatus is a separatory funnel, shown in half size in accompanying figure with an inwardly projecting tube, A. The bore of the stopcock should preferably be as large as shown. A No. 18 platinum wire is sealed in at B.



The apparatus is filled with mercury to within 1 or 2 mm. of the end of tube A, which itself is completely filled with mercury, and electrical connection is made to the negative terminal of the battery. The anode may have any of the usual rotating forms. The electrolyzing vessel is conveniently supported by an iron ring clamped to the stand carrying the motor for rotating the anode. When electrolysis is completed the anode is brought as close as possible to the surface of the mercury without short-circuiting, and the electrolyte is allowed to run out by opening the stopcock. The washing is done very easily by a jet of water from a wash-bottle, leaving the stopcock open during the operation, the course of the washing being followed by the ammeter.

If a rotating anode is used the electrolysis is accomplished in 15 or 20 minutes. The mercury may be used over and over again without purification; this is another advantage of removing the excess of precipitant before electrolysis, for the amount of foreign material going into it is thus reduced to a minimum. When a stock of mercury saturated with iron and chromium has accumulated it may be purified by the rapid method of Hildebrand.² A fair degree of purification can be attained in a few minutes by shaking in a separatory funnel with concentrated hydrochloric acid.

ANALYTICAL DATA.

Table I gives some results that have been obtained on synthetic mixtures of chromium, vanadium and iron. The vanadium was added from a stock solution of sodium vanadate which was carefully standardized by reducing several portions with sulphur dioxide and titrating against permanganate; the iron was from a sulphuric acid solution of a Bessemer steel with 0.1 per cent. carbon, and the chromium from a roughly standardized chrome-alum solution. Precipitation by cadmium carbonate was made in the presence of 4 grams of iron, one-half of the solution of the precipitate being used for electrolyzing.

TABLE I.
Vanadium.

Number.	Present.	Found.	Error.	Chromium.
1.....	0.0030	0.0030	0.0000	0.0286
2.....	0.0030	0.0030	0.0000	0.0572
3.....	0.0101	0.0102	+0.0001	0.0358
4.....	0.0117	0.0116	-0.0001	0.0286
5.....	0.0199	0.0204	+0.0005	0.0572
6.....	0.0376	0.0371	-0.0005	0.3150
7.....	0.0407	0.0410	+0.0003	0.3150
8 ²	0.0010	0.0010	0.0000	none

Determinations were made on the vanadium steel standard of this Bureau, first, from hydrochloric solution; second, from sulphuric solution. Duplicates gave 0.145 per cent. vanadium and 0.142 per cent. vanadium from the hydrochloric solution. To these there had been added 0.0750 gram and 0.1064 gram chromium respectively. In sulphuric solution, there was obtained 0.145 per cent. The mean of several very careful determinations by Bureau chemists, using different methods, was 0.143 per cent. On the new chrome-vanadium standard now in preparation

¹ *J. Am. Chem. Soc.*, **31**, 933 (1909).

² In presence of 10 grams of iron.

¹ "Electroanalysis," fourth edition.

the method gives 0.203 per cent. and 0.203 per cent. The averaged complete analysis of the vanadium standard and of the chrome-vanadium standard (full data for the latter have not yet been received and the analysis given is not final) are shown below.

TABLE II.

Standard.	C.	Si.	P.	S.	Mn.	V.	Cr.	Ni.	Cu.	Mo.
Vanadium.....	0.350	0.303	0.035	0.027	0.669	0.15	0.007	0.009	0.022	0.006
Chrome-vanadium....	0.377	0.113	0.043	0.029	0.58	0.197	1.36	0.15	0.056	...

The results show that a satisfactory degree of accuracy is attainable; this may be increased even more, if desired, by using a larger sample of the steel, for there is no reason why the vanadium should not be concentrated from 10 grams or more of steel, if desired. The minimum amount of vanadium here determined equivalent to 0.01 per cent. in a steel (No. 8 of Table I) shows how delicate the method is; the maximum amount (No. 7 of Table I) shows the possibility of using cadmium precipitation, followed by electrolysis, for high vanadium products. The complete and quick precipitation of large amounts of chromium by cadmium carbonate is equally striking; a method for determining chromium in various kinds of steel, based upon these observations, is being worked out in this laboratory.

From what has been said of the effect of the presence of other substances when titrating hypovanadate solutions with permanganate it is evident that a method like this has distinct advantages in eliminating other metals. If the method is to be used for other steels than those for which it was devised, the effect of other metals must be considered. Such metals as copper and nickel would not interfere. The behavior of molybdenum and tungsten in appreciable amounts has not been investigated, but molybdenum, if at all precipitated by cadmium carbonate, may be eliminated during the hydrogen sulphide precipitation of the excess of cadmium. Tungsten might be removed by evaporation of the cadmium precipitate with nitric acid, followed by filtration. After conversion of the nitrate to a sulphate solution electrolysis could follow as above described. Titanium would probably be precipitated by the cadmium and remain with the vanadium through the electrolysis; however, it would not be reduced by sulphur dioxide nor hydrogen sulphide. These points will be investigated as opportunity permits.

SUMMARY.

(1) Various errors in the usual methods for determining vanadium in steel are pointed out and in a few cases methods for correcting or eliminating these are indicated.

(2) A short and accurate method for determining vanadium in vanadium and chrome-vanadium steels is discussed and described.

The writer is indebted to Doctor Hillebrand for many helpful suggestions during the course of this investigation.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

A RECENTLY DISCOVERED BACTERIAL DECOMPOSITION OF SUCROSE.¹

By W. L. OWEN.

Received March 10, 1911.

The knowledge of the association of bacteria with the fermentation of saccharine fluids is most probably as old as the science itself. Although the investigations that led to the discovery of bacteria by Antony Leuwenhoek, who is known as the father of bacteriology, were most likely actuated by his interest in microscopy rather than biology, yet it is but natural to assume that the study of fermentation must have had a great influence upon bacteriological investigations. Almost a century elapsed after the immortal Leuwenhoek's discovery of unicellular life before the importance of his achievement was sufficiently realized to direct the attention of other investigators to the subject. It was during the middle of the nineteenth century, at the time when discussions of the nature of fermentation were at the highest point and were interesting the great chemists of that day, when the investigations that paved the way to modern bacteriology were conducted. The wide-spread interest in the subject of fermentation during that period must have given great impetus to the development of the science of agricultural bacteriology, the science which in its comparatively brief period of existence has contributed untold blessings to mankind. It is particularly interesting to trace the influence of the alcoholic industry upon the science of bacteriology, for it shows that as it was various speculations regarding the decomposition of sucrose that gave birth to the science of bacteriology, so this science has in turn been recently applied to explain a new decomposition to which sucrose is susceptible. The evolution of the alcoholic industry, from its infancy in the earliest history of mankind to its present state of scientific perfection, has been intimately associated with notable discoveries in bacteriology. It was in the investigation of various phases of the alcoholic industry that many new discoveries were made of the products of bacterial action. As the manufacture of alcohol became more scientific it was but natural that greater attention was paid to the investigation of various species of bacteria in their relation to fermentation of sugars. As a result of the interest created by the alcoholic industry in the bacterial action upon sugars the various products of this action became widely known and methods were rapidly evolved to prevent the destructive activities of bacteria upon the fermentation of alcohol. The bacteriological investigations of the fermentation of sugars were chiefly concerned, however, with the discovery of the species of bacteria that were particularly inimical to the process of alcoholic fermentation by yeasts, and as soon as methods were discovered to overcome this trouble further investigations were unnecessary and consequently unpopular. At the time when these investigations were regarded as of only indirect interest in the fermentation indus-

¹ Read before the Louisiana Section, Am. Chem. Soc., Feb. 17, 1911.

try, the investigations of the action of yeasts upon sugars were vigorously conducted.

During this period of investigative activity, the enzyme invertase which causes decomposition of sucrose into dextrose and levulose was isolated from yeast by Berthelot, but a quarter of a century elapsed after this discovery before Buchner successfully isolated zymase, the enzyme causing alcoholic fermentation. As a result of these researches the subject of alcoholic fermentation was well understood in all its various phases, and attention was again directed to the investigation of the bacterial decomposition of sucrose. The action of bacteria on that particular group of sugars which are known as the hexoses having been quite thoroughly investigated, many scientists began to occupy themselves with the study of bacterial action on sucrose. About this time interest in the question of the ability of bacteria to invert sucrose was renewed, and a number of investigations were conducted upon the subject. Prominent among the investigators of the subject are the names of Fermi and Montesano, who after very exhaustive researches concluded that only a very few bacteria had the power of breaking down sucrose into dextrose and levulose through inversion. Thus it will be seen that the investigation of the subject of bacterial action upon sucrose did not result in discovering any appreciable power on the part of these microorganisms to bring about a decomposition of this material. The work of the above-named authors, applying as it did to a great many species of bacteria under a great variety of conditions, did not tend to prove very convincing of the ability of bacteria to induce deterioration of sucrose by this means. Unlike the alcoholic industry, the sugar industry has only in comparatively recent years been sufficiently concerned with the dangers of bacterial fermentation to promote any definite lines of investigation upon this subject. On that account the sugar industry had not until recently been the means of extending our knowledge upon the subject of bacterial action upon sucrose. From time immemorial the sugar manufacturers doubtless realized the danger from bacterial fermentation, but owing to the fact that few of these products are very susceptible to such deteriorative changes of the sort, and as such products are seldom exposed to the action of bacteria for any great length of time, such dangers as have existed have been quite readily overcome. The sugar maker, just as the alcohol manufacturer, is concerned with bacteriology only insofar as it may enable him to prevent the access of these microorganisms into his products; but as the manufacture of alcohol necessitates both longer exposures to bacterial action and working with products very much more readily fermented than in case of the sugar products, the alcohol manufacturers have been compelled to give more attention to the subject. The sugar maker has been accustomed to regard his sugars as products beyond the reach of his microscopic enemies, and when his raw product—the cane juice of the mill—has reached the stage of crystallized sugar it is, as he thinks, no

longer susceptible to bacterial fermentation. It is highly probable, however, that cases of the deterioration of sugars were observed even in the earliest times. It is certainly very reasonable to suppose that bacteria have been developing in sugars for many ages, but it has been so customary to attribute a fall of the polarization of sugars to lack of uniformity in sampling or to other causes of the kind, that not until very recently has the true nature of the deterioration been suspected. Owing to the prevalent opinion, not only on the part of the sugar manufacturer, but also on the part of scientists in general, that sugars are not favorable media for bacterial development the true cause of the deterioration in sugars remained unsuspected for a long time. It is only fair, therefore, to the sugar manufacturer, to say in his behalf and in defense of his scientific knowledge, that he had many inferences of a scientific nature to justify him in his belief that bacteria could not develop in sugar. So prevalent has been this opinion that we have been accustomed to look upon sugar more in the nature of an antiseptic than a product susceptible to bacterial action and so confirmed have we been in this idea that we have in many cases been in the habit of using sugars in the preservation of food products as one might use an antiseptic. Indeed, the preservative properties of sugars have been so widely talked of that we might have had reason to entertain the fear that some of our over-enthusiastic pure food authorities might place that product under the ban of the law and might forbid its use, owing to its supposed preservative properties.

About ten years ago the various theories of the deterioration of sugar developed into exact knowledge of this phenomenon and it was found that bacteria were associated with and found to be the cause of this phenomenon. At a little later period the various organisms found in sugars were isolated and their characteristics thoroughly studied. In the early investigations of the subject the Sugar Experiment Station took a prominent part, and the investigations there conducted were doubtless responsible for much of the research of the kind that followed. The earlier investigations of this subject attracted much attention, and as the great possibilities of this field of investigation were revealed a research of this kind was instituted in various parts of the sugar world. As a result of the early investigations that had been instituted at the station, a Department of Bacteriology was established in 1908 with the view of taking up as a matter of first importance an investigation of the deterioration of raw sugars. Accordingly, investigations of the subject were promptly instituted and the results of the two years' work—of which this paper is a summary—have recently been issued in bulletin form. Every investigation of bacterial action must necessarily take an account of the following factors: (1) The species of microorganisms associated with the action and their various characteristics; (2) the nature of the action and the conditions affecting it. By applying this general plan to our investigations on the deterioration of sugars we began

by making a thorough study of the bacterial flora of many different grades of sugars. These sugars were procured from the most important sugar-producing countries, and as they represented various climatic conditions and manufacture, it was thought that a study of them would afford adequate data as to the occurrences and distribution of the deteriorative type of bacteria. The species isolated were accordingly studied and were found to be, not as we might have supposed new and unusual numbers of the bacterial kingdom, but old species that had been isolated and studied many years ago. They might be considered as old friends in new surroundings, for they belong to that well known group of bacteria known as the potato bacilli, the members of which are the *Bacillus vulgatus*, *Bacillus mesentericus fuscus*, *Bacillus mesentericus ruber*, *Bacillus mesentericus niger*, *Bacillus mesentericus granulatus*, and are characterized by the very high resistance of their spores to heat. In their newly discovered habitat these organisms were found to have lost little of their old characteristics, and if anything seem to have developed even greater resistance to heat. Our experiments upon this property show that organisms seemed even more resistant as isolated from sugars than when they are taken from the soil. It is very probable that the exposures to the various temperatures incident to sugar manufacture have been responsible for their great resistance. It was found that the deteriorative type of organisms which occurred in cane juice were not destroyed by the various temperatures to which the product was subjected and would be found in the sugar as soon as it dropped from the centrifugal. In order to test the resistance of the spores to bacteria at high temperatures we conducted experiments in the laboratory under conditions where the exposures might be regulated with absolute precision. In the table is given the results of this experiment.

RESISTANCE OF SPORES TO HEAT.

CoH.	Temperature 212° F.				Temperature 230° F.			
	15"	30"	60"	120"	5"	15"	30"	60"
<i>Bac. vulgatus</i>	—	—	+	+	—	+	+	
<i>Bac. vulgatus</i> (B)...	—	—	—	+	—	—	+	
<i>Bac. vulgatus</i> (C)...	—	—	—	+	—	+	+	
<i>Bac. vulgatus</i> (D)...	—	—	—	—	—	—	+	
<i>Bac. mes. ruber</i>	—	—	—	—	—	—	+	
<i>Bac. mes. fuscus</i> ...	—	—	—	—	—	+	+	
<i>Bac. mes. fuscus</i> (A)...	—	—	+	+	—	+	+	
<i>Bac. mes. fuscus</i> (B)...	—	—	+	—	—	—	+	
<i>Bac. mes. niger</i>	—	—	—	+	—	—	+	
<i>Bac. liodermos</i>	—	—	—	+	—	—	+	
<i>Bac. mes. granulatus</i> ...	—	—	—	+	—	—	—	
<i>Bac. gummosus</i>	—	—	—	+	—	+	+	
<i>Bac. megatherium</i>								
(A).....	—	—	—	+	—	—	+	
<i>Bac. sacchari</i>	—	—	+	+	—	+	+	
<i>Bac. megatherium</i>								
(B).....	—	—	+	+	+	+	+	

+ indicates spores killed.
 — indicates spores capable of germination.

These results show that the spores in some cases could vegetate after several hours' exposure to the temperature of 212°. As the deteriorative type of bacteria are very widely distributed in nature and are always to be found around sugar mills, and as we have

seen from their resistance to high temperatures that they will readily survive the temperature reached in sugar manufacture, we need not wonder at the sources from which sugars become contaminated. The species found in sugars occur almost everywhere, so it is very likely that no sugar house will be free from these organisms. In order to actually determine the various avenues of contamination of sugar products and to learn of the bacterial content of these products during their manufacture, we instituted bacteriological control experiments in the sugar house at various periods during the grinding season. From these experiments we found that the deteriorative type of organisms occurred in all of the product, from the juice to the finished sugar, and were to be found on the canes, in the yards, and in the dust of the buildings. We might say that wherever sugar products are exposed to the air that they would be more likely to become contaminated with this type of organism than from any other species known.

In the following tables are given the bacteriological analyses of the various products in the sugar house, and also in the sugar refinery.

AVERAGE OF RESULTS FROM BACTERIOLOGICAL CONTROL WORK AT THE SUGAR HOUSE OF THE EXPERIMENT STATION, SEASON 1909—NINE "RUNS."

Product.	No. of organisms per gram or cc.	Species.	Presence of species of economic importance.
Raw juice.....	280,000	Yeasts, molds, bact.	+
Sulph. juice.....	35,000	Yeasts, molds, bact.	+
Limed juice.....	37,500	Bact. predominating	+
Defecated juice....	750	Sugar group, bact. E	+
Syrup.....	400	Sugar group, bact. E	+
Massecuite.....	450	Sugar group, bact. E	+
Sugars.....	600	Sugar group, bact. E	+
Molasses.....	35,000	Mixt. contam.	+
Wash water.....	25,000	Mixt. contam.	+
Filter press cake....	1,500,000	Mixt. contam.	+

BACTERIOLOGICAL ANALYSIS OF SAMPLES FROM A REFINERY.

Name of sample.	Dilution employed.	No. of organisms per gram or cc.	Presence of species of economic importance.
Raw sugar.....	1 : 100	1,000	+
Raw washings.....	1 : 1000	5,000	+
Washed sugar.....	1 : 100	2,000	+
Melted washed sugar.....
Def. wash sugar and liquor	1 : 200	800	+
Bag filt. wash sugar and liquor.....	1 : 1000	3,000	Moulds and bacteria
Light sweet water.....
Clear filtered liquor.....	1 : 1000	1,000	+
Defecated washings.....	1 : 000	6,000	+
Bag filtered washings.....	1 : 000	5,000	+
Dark sweet waters.....	1 : 2000	8,000	+
Char filt. washings.....	1 : 400	8,000	+
Mud water.....	1 : 2000	400,000	+
Press cake.....	1 : 2000	No development	
Press water.....
Conc. sweet water.....	1 : 1000	20,000	+
Granulated magma.....	1 : 100	300	+
Granulated syrup.....	1 : 1000	5,000	+
Wet granulated sugar.....	1 : 50	150	+
Dry granulated sugar.....	1 : 50	150	+
Remelted magma.....	1 : 50	200	+
Remelted syrup.....	1 : 1000	25,000	+
Undefecated liquor.....	1 : 500	10,000	+
Remelted sugar.....	1 : 500	500	+
Car sugar.....	1 : 100	3,000	+
Barrel syrup.....	1 : 100	8,000	+
Car syrup, two weeks in hot room.....	1 : 100	400	+

It is interesting to note that on an average of ten runs in the Experiment Station sugar house, there was a decrease of approximately 87 per cent. of the organisms occurring in the sulphured juice over the number of organisms occurring in the raw juice. This is very likely to be attributed to the precipitation of the sulphitation process rather than to the germicidal action of the sulphurous acid. After investigating the bacterial flora of sugars quite thoroughly and learning of their various characteristics, it was next necessary to investigate the nature of this action upon sucrose. We endeavored, therefore, to determine the exact means by which these organisms caused decomposition of sucrose. Was the deterioration of sucrose due to an invertase action exercised by the bacteria, or was it new decomposition? As the decomposition of sucrose into dextrose and levulose by the enzyme invertase was the only decomposition to which this substance was known to be susceptible by microorganisms, it was but natural for investigators of the subject to attribute the deterioration of sugars to this action. Such a theory of the nature of the deterioration of sugars is not exactly in accord with what has been found to be true as to the condition governing inversion by invertase. In the first place, the concentration of sucrose in the film of moisture, surrounding the crystals of sugar, is too high to be favorable for such action, and in addition to this, unfavorable conditions of concentration bacteria, as we have previously observed, have never been known to be very active in causing inversion of sucrose. In the premises of the case, therefore, it would seem that the deterioration of sugars by bacteria must be due to some other action upon sucrose, and if this action is not due to the secretion of invertase, how shall we explain it? For evidently we have no precedent in the subject to which to attribute it.

A few years ago an investigator of this subject discovered that bacteria isolated from sugar had the power of inducing what he termed gum fermentation of sucrose solution. This author isolated the gum thus formed and gave it the name of *Levan* on account of its levorotary nature. This investigator was Greig Smith, a bacteriologist in New South Wales, and his work attracted considerable attention at that time. According to this author the origin of this gum was sucrose, but this substance had to be transformed by the inverting action of the bacteria into dextrose and levulose before it could be converted into levan. It seems never to have occurred to him that levan was formed to any extent by these organisms in raw sugars, so he was very probably under the impression that the deterioration of sugars was due to the inverting action of the organisms rather than the gum-forming action, which he himself had discovered in sugar solution. Smith very likely supposed that the action of the bacteria upon sucrose in raw sugars were confined to inverting the sucrose, while in sugar solution their action extended to the gum fermentation of the invert sugars thus formed. It will be quite unlikely, it seems, for the

same bacteria to exercise a different action upon raw sugars from that which had been found to take place in solution. Our experiments in determining the rate of deterioration of sugars under the natural conditions and under conditions of artificial inoculation yielded certain results which indicated that certain bodies must have been formed which introduced an error in our analytical work. In many cases we found, to our surprise and great astonishment, that our Clerget analyses on sugars showed an increase rather than a decrease of sucrose. From many of these analyses it appeared that sugars, not unlike whiskey, tend to improve on storage. As measured by the single polarization, the sugars were deteriorating very rapidly. To what then was this discrepancy between single polarization and the Clerget method due? These results were too constant to attribute them to any incidental error in manipulation. We soon found this to be the rule rather than the exception in our sugar analyses. The formula for determining sucrose by the Clerget method of analysis is based upon the fact that in the inversion by hydrochloric acid none of the optically active bodies present other than sucrose shall have their respective readings increased or decreased in the process. The reliability of the method depends, as you all know, upon the fulfilment of these conditions. Any body, therefore, that may be present in the sugar and which would have its optical activity either increased or decreased or changed in regard to its original direction of rotation by the hydrochloric acid inversion would necessarily introduce an error in the analysis. So it was that the increase in our Clerget analysis over the single polarization suggested to us the fact that some optically active body had been formed in the sugars that we were investigating. As the organisms found in sugars have been found to possess the power of forming gum levan from sucrose, it was the formation of this gum that was suspected to be responsible for the increase in sucrose as determined by the Clerget method of analysis. Levan having an optical activity of about 40 becomes hydrolyzed through the inversion with hydrochloric acid, and the levulose has an optical activity of about 89.2. This increase in optical activity will very readily account for the error in the analytical determination. In order to overcome this difficulty we endeavored to devise some method of bringing about the inversion for invert reading by some other means than ordinary hydrochloric acid methods. In certain cases the use of prepared invertase has been recommended for this inversion and it was thought that if this substance was found to have no action on levan it could be used with very satisfactory results. It has been our experience, however, in using invertase that so much care is necessary in order to attain the exact point of acidity necessary for the complete inversion of the substance that it is impracticable to use this method to any great extent.

Mr. W. G. Taggart, of the Sugar Experiment Station, who as the assistant chemist has been in charge of the analytical work of this department, has prepared

considerable data on the influence of levan on the analysis of sugar, as well as the results of his experiments with the invertase method of sucrose determination. I feel quite certain that he will be only too glad to give you the facts of his experiments should you desire them.

As an example of the influence of levan on the analysis of sugars, we give the following results from the analyses of sugar samples:

	Single polarization.	Sucrose (Clerget.)	True sucrose invertase method.
Sample No. I, refined sugar	99.98	99.99	99.98
Sample No. II, Inoculated solution containing gum	0.00	0.8	0.17
Sample No. III, Peruvian crystals	91.20	95.0	91.4
Sample No. IV, from Gramerey	87.0	89.82	87.6

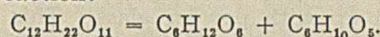
It is interesting to note the difference in sucrose (Clerget), and the single polarization. In the analyses of solutions containing 10 per cent. of sucrose which were undergoing a gum fermentation by the micro-organism investigated, a comparison between the single polarization and the Clerget and the true sucrose (corrected Clerget) are as follows:

EXPERIMENT NO. VII.—GUM DEVELOPMENT AS AFFECTED BY DURATION OF INOCULATION PERIOD. CULTURE USED, *BACILLUS VULGATUS*.

Age of cult. Days.	Acidity 25 grams required, Reducing		Single polarization.	True sucrose (corrected)		
	Cc. N/10.	sugar.		Clerget.	Clerget.	Gum.
..	9.2
2	2.50	2.33	5.6	6.74	6.04	1.05
4	2.80	5.56	2.0	4.83	3.65	1.77
6	6.78	0.0	2.30	0.11	3.28
8	2.80	7.28	-0.4	2.30	0.76	2.82
10	2.6	6.90	-0.4	1.63	2.59
13	2.6	6.90	-1.3	1.85
15	2.3	7.14	-1.2	1.35	1.98
17	2.2	7.14	-1.3	2.36
20	2.4	7.14	-1.3	1.66	1.34
22	2.1	7.14	-1.8	1.25	1.88
28	3.0	7.84	-1.8	1.16	(2.37)
34	3.2	7.28	-2.1	1.00	1.69
42	3.6	7.84	-2.2	0.26	0.65

From this table it will be noted that all the sucrose was really destroyed by the eighth day, as shown by the corrected Clerget, while by the ordinary Clerget method the sucrose readings were obtained as long as 42 days. The true sucrose was computed by correcting the Clerget analysis upon the basis of the influence of the amount of gum formed in the solution. Although convinced by the great amount of evidence that was at hand that levan was present in the sugars and that it was responsible for the analytical errors, we could not succeed in separating it in such a state of purity as would permit of its identification in those sugars where it was strongly suspected. Precipitation with alcohol brought down so many impurities that it was impossible to separate the gum to a point where it could be definitely identified. We were often successful to the point of obtaining levorotary precipitates, but the other properties of levan were lost. In order to prove, however, that our failure to isolate levan from the sugars in which we suspected it was not proof of its absence, we

sometimes added small quantities of the gum to these sugars and failed to recover it by alcoholic precipitation. It seems evident that gum formation takes place in sugars, and it is this means by which the organisms occurring therein cause decomposition of the sugars. We have already noted the fact that the conditions obtaining in sugars are not all suitable for the action of invertase. It was found that the formation of levan could take place only where there was sucrose present. Invertase has been found to be most active in an acid solution and entirely inactive under alkaline conditions. Just the reverse we have found to be true of the formation of levan, which seems far more energetic in a slightly alkaline solution. We were not able to produce it from dextrose and levulose or from a mixture of these two sugars, and as we have found the presence of sucrose to be essential to the formation of gum, and as its decomposition into gum is most active under conditions known to be unfavorable for inversion into dextrose and levulose, it seems evident that micro-organisms must have the power of decomposing sucrose into gum and reducing sugar direct. Since reducing sugars are always found to develop concurrently with levan in this fermentation of sucrose, we must conclude that these two substances are both formed in the fermentation. This newly discovered decomposition takes place according to the following reaction:



Greig Smith, the bacteriologist, who made quite an investigation of the gum fermentation of sucrose, advances the theory that levan was formed from sucrose indirectly. He claimed that the organism first inverted sucrose and from the nascent dextrose and levulose thus formed the organism produced the gum levan. This author very probably arrived at this conclusion because he found the organism was not able to produce the gum in those sugars in their natural condition. He naturally concluded therefore that those sugars possessed some quality when in the nascent stages that made them favorable for the gum fermentation. In order to disprove this theory of the formation of levan from nascent dextrose and levulose, we conducted experiments upon sugar solution inoculated with both gum-forming bacteria together with yeast. In these experiments we found that the formation of gum where bacteria were used alone was much greater than where both yeast and bacteria were used together. If nascent levulose and dextrose were the origin of the gum we should have expected much greater gum formation to have taken place where the yeasts and bacteria were used. As yeasts have greater inverting power than bacteria, there should have been more invert sugar formed in that condition than where bacteria are used alone. A microscopical examination of the solution showed an abundance of yeast cells and bacteria in the solution in a flask which was inoculated with both classes of micro-organisms. A chemical analysis also showed that much more reducing sugars had been formed where the yeasts were used, so that if the Smith theory

was right, conditions were certainly more favorable for gum formation than where the bacteria were used alone. But, as a matter of fact, there was almost twice as much gum formed in a flask containing the bacteria as in the one in which yeasts also were used. It appeared evident that the sucrose inverted by the yeasts was no longer favorable for gum formation. These results indicate very strongly that nascent levulose and dextrose were not the origin of the gum. In consideration of the facts therefore that gum formation takes place only where sucrose is present, and as this action seems to be accelerated in conditions of concentration of medium and alkalinity of the solution known to be unfavorable to invertase, it seems evident that we are here dealing with an absolutely new decomposition of sucrose. This belief is further strengthened by the fact that bacteria have never been found to invert sucrose to any great extent, and that the nascent products of inversion seem to be no more favorable to gum formation than dextrose and levulose in their natural state. We have succeeded in isolating the enzyme causing the decomposition of sucrose by growing cultures of the bacillus *vulgatus* on agar agar in large moist chambers and taking the surface growth after about ten days old, we found that we could use this growth after the bacteria had been killed by an antiseptic with the same results as from the living cultures. The large mass of growth was usually spread upon the surface of a plate and ground up with powder glass. This pulverized mass was then dissolved in water and precipitated with alcohol. By this method we obtained a dark powder which, when introduced into a sugar solution containing sufficient toluene to prevent bacterial growth, induced an active gum formation just as when the living cells of bacteria are used. In these experiments a microscopical examination shows that there were no living cells developing in the solution, so that any changes that had taken place must have been due to an enzyme. It was, however, found in experimenting with this bacterial extract that gums and reducing sugars were formed, which is further proof of the correctness of our theory as to the decomposition of sucrose in the gum and reducing sugars. For this new enzyme we have proposed the name *levanase*, and are now engaged in investigating its properties in the laboratories of the experiment station.

In conclusion, I would say to the members of this scientific society that the facts presented in this paper should naturally direct your attention to means of obtaining more reliable methods than are now available for the determination of sucrose. The investigation herein reported is convincing of the fact that practically all of our unrefined sugars are contaminated with the sucrose-decomposing bacteria. On this account the sucrose is continually subject to this action which might readily account for the many litigations regarding discrepancies in analyses that are so current at this time. Were the deterioration of sugars due to the breaking down of sucrose into dextrose and levulose, as is the case in direct inversion,

we would have no reason to concern ourselves with the elaboration of new methods, for in that case our present Clerget would suffice. But in the light of this discovery of the transformation of sucrose into reducing sugars and an optically active gum, which is very likely of a transitory nature, we must agree that under such conditions our present methods of sucrose determination are very unreliable and ought to be improved upon.

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EXTRACTION OF GRAINS AND CATTLE FOODS FOR THE DETERMINATION OF SUGARS: A COMPARISON OF THE ALCOHOL AND THE SODIUM CARBONATE DIGESTIONS.

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Received April 10, 1911.

INTRODUCTION.

There has been some discussion among chemists as to methods of determining sugars in agricultural products, such as grains, plants, both dried and fresh, and cattle foods. Figures obtained by different chemists on the same sample varied many times by 1 per cent. or more. This wide variation in results was also noted when the same chemist used different methods or made a slight modification of his own in a printed method. The difficulty experienced was not so much in the actual determination of the sugar as in the solvent and the method of procedure used to obtain an extract on which to work. Again, sometimes the results obtained on one day could not be duplicated on the same sample at a later date. Often this may be attributed to lack of homogeneity of the sample, a fault remedied by better preparation of the material, especially by finer grinding. But the chief difficulty appears to lie in the changes due to enzymic action during or after extraction and also somewhat to the solvent and the clarification agents used. In this class of material, sugars are usually present in small quantities and the other carbohydrates, such as starch, pentosans, gums, etc., in much larger amounts. It is because of the latter substances that the usual water methods for sugar-beet analysis can not be successfully used.

LITERATURE ON THE SUBJECT.

The literature contains but few definite methods for the determination of sugars in grains, although alcohol is often spoken of as the solvent used for extracting materials, especially when sugars are to be obtained. Other references are found to the determination of sugars in the water extract of the material. In the early methods¹ of the Association of Official Agricultural Chemists, the procedure was to "stir 3 grams of the sample in a beaker with 50 cc. of water for an hour," filter, and make up to volume. This procedure gave varying results, depending upon the temperature of the water during extraction and the fineness of the material. Later this procedure was modified by using ice water for extraction and submerging the beaker during extraction into a bath

¹ U. S. Dept. Agr., Bureau of Chemistry, Bull. 46, 24.

of broken ice.² In a majority of cases this does not wholly accomplish its purpose, namely, to stop enzymic action and thereby insure concordant results. It is a rather cumbersome procedure, and while enzymes may be inhibited during extraction, they become active again when the filtration is carried on at room temperature. However, many now use this method of procedure for preparing the extract for sugar determination. The official methods offer as an alternate for the water method an extraction with 40 or 50 per cent. alcohol, but no definite procedure is outlined.

O'Sullivan, as early as 1886, was using alcohol to extract barley for the determination of the quantity and kind of sugars present. He states this to be the usual method of determining sugars at that time. Stone,³ in 1897, published a method for "The Quantitative Determination of Carbohydrates in Food-stuffs," in which he extracted successively with boiling alcohol, cold water, diastase or malt infusion, dilute hydrochloric acid, and finally 1.25 per cent. sodium hydroxid. The alcohol treatment was for the removal of the true sugars, the cold water for the removal of dextrin and soluble forms of starch. Brown⁴ published results obtained on a distillery waste by this method, but beyond this little mention of it could be found.

M. N. Straughn, when working with C. G. Church on the sugar content of dried sweet corn at the Maryland Experiment Station in 1902, tried many modifications of the water extraction and alcohol extraction methods. In this product sugars were present in small quantities together with a large percentage of starch, and the enzymes were active, as the drying had been carried on at a low temperature. On extracting this material with cold water great difficulties were experienced in obtaining clear extracts and a rapid filtration. It was soon found that the percentage of total sugars obtained by this method increased with the length of time of extraction, or, if the time of extraction was fixed, the results varied with the time consumed in filtering. This increase was no doubt due to enzymic action. Extraction with hot water could not be practiced, as the material gelatinized, some becoming soluble, and filtration was almost impossible.

Alcoholic digestion was then tried. By this method duplicate results were obtained on different days, and there was an agreement of results whether cold or hot solvents were used, although with cold extraction great difficulty was experienced at times in filtering, but even under these circumstances the results of the sugar determination in the extract, provided evaporation was guarded against, were practically the same. In a study made on the "Influence of Environment on the Composition of Sweet Corn,"⁴ the alcohol digestion method was used.

The sugar laboratory in 1905 conducted a long series of experiments on the various methods of extraction and the solvents to be used for dissolving the

sugars from grain. The results confirmed those of Church and Straughn on the whole. It was found that 50 per cent. alcohol was the best solvent and that the extraction should be carried on hot. At this strength it was noted that all enzymic action seemed to be stopped and the extracts were easily filtered. The method was tried on many dried plants, grains, and numerous other materials sent to this laboratory for examination. Slight modifications have been made in the procedure of the method from time to time, and its final statement is given in the following section.

STATEMENT OF ALCOHOL DIGESTION METHOD.

Place 12 grams of material in a 300 cc. graduated flask,¹ add 150 cc. of 50 per cent. alcohol by volume (carefully neutralized), mix thoroughly, and boil on a steam bath for one hour, using a small funnel in the neck of the flask to condense the vapor. Then cool. If desired, allow it to stand over night. Make up to volume with 95 per cent. alcohol (neutral in reaction), mix thoroughly, allow to settle, transfer 200 cc. to a beaker with a pipette, and evaporate on a steam bath to a volume of from 20-30 cc. The presence of a trace of alcohol is not harmful. Do not evaporate the solution to dryness. (By evaporating the 200 cc. portion in a short-necked, balloon-shaped distilling flask, connected with a condenser, 75-80 per cent. of alcohol can be recovered before the material in the flask foams violently. The short neck—1 inch—of these flasks makes it possible to remove the residue easily. The 100 cc. remaining in the digestion flask may be strained through a cotton bag and the alcohol recovered from the liquid as just described. This is easily accomplished and results in a marked saving when a large number of samples are run.) Transfer the contents of the beaker or flask, as the case may be, to a 100 cc. graduated flask, washing thoroughly with water. Add enough of a saturated solution of neutral lead acetate to produce a flocculent precipitate, and allow to stand 15 minutes. At this point the solution may safely stand over night if desired. Make up to the mark with distilled water and pass through a folded filter, carefully saving all of the filtrate, to which add enough anhydrous sodium carbonate to precipitate all the lead, allow to stand 15 minutes, and pour onto an ashless filter. Over 75 cc. of filtrate should be obtained. Test the filtrate for lead with a small quantity of dry sodium carbonate, and if any precipitation occurs add more anhydrous sodium carbonate and re-filter. Use 25 cc. of this clear filtrate together with 25 cc. of water for the determination of reducing sugars by the method of Munson and Walker.² In a 100 cc. graduated flask, place 50 cc. of the same filtrate, add a small piece of litmus paper, and neutralize with acetic acid; then add 5 cc. of concentrated hydrochloric acid, and let stand over night for inversion. (Standing 48 hours does not apparently affect the results.) Then pour the inverted solution into a 400 cc. beaker and neutralize with anhydrous sodium car-

¹ If the material is acid in reaction, it would be well to add from 1-3 grams of precipitated calcium carbonate to neutralize the acidity.

² U. S. Dept. Agr., Bureau of Chemistry, Bull. 107 (revised), 241.

¹ U. S. Dept. of Agr., Bureau of Chemistry, Bull. 107 (revised), 57.

² J. Am. Chem. Soc., 29, 183 (1897).

³ *Ibid.*, 23, 229 (1901).

⁴ U. S. Dept. Agr., Bureau of Chemistry, Bull. 127.

bonate; return it to the 100 cc. flask and make up to the mark. Filter, if necessary, and use 50 cc. for the determination of total sugars as invert by the method of Munson and Walker.¹

The amount of cuprous oxid or copper obtained (see page 489) in either the reducing or the total sugar determination represents the sugar contained in 2 grams of the material. Therefore the weights of the invert sugar divided by 2 and multiplied by 100 give the respective per cents. of sugar as invert. Subtract the per cent. of reducing sugars before inversion from the per cent. of total sugar after inversion, both calculated as invert, and the difference multiplied by 0.95 gives the per cent. of sucrose (see page 491 for expression of results). Since the insoluble material of the grain or cattle food occupies some space in the flask as originally made up, it is necessary to correct for this volume. Results of a large number of determinations on various materials have shown the average volume of 12 grams of material to be 9 cc.; therefore the correction factor for 12 grams in 300 cc. is 0.97, and the percentage figures for reducing sugar and sucrose are to be multiplied by this factor to obtain the true amounts.

STATEMENT OF SODIUM CARBONATE DIGESTION METHOD.

Lately the cold-water extraction method has been improved. Realizing that the trouble experienced with this method of extraction was largely due to the activity of enzymes, it was suggested that a small percentage of sodium carbonate be added to the water used for extraction to inhibit their action.² Based upon this suggestion, a method was devised which in the case of certain grains gave figures which checked with those obtained by the alcohol digestion. The procedure is as follows:

Place 8 grams³ of the finely ground grain in a 250 cc. flask and add 190 cc. of a 0.2 per cent. solution of sodium carbonate. Allow to stand at room temperature for two and one-half hours, shaking intermittently. At the expiration of the time add 10 cc. of a hot saturated potassium alum solution; shake and filter. Use 25 cc. of the solution, the equivalent of 1 gram of material, for reduction by Allihn's method,⁴ calculating the cuprous oxid obtained (see page 489) to dextrose by Allihn's table. To 50 cc. of the solution in a 50-55 cc. flask, add 5 cc. of concentrated hydrochloric acid and allow to stand over night for inversion. Then neutralize the whole solution with sodium carbonate, make up to 100 cc., and in 25 cc. of this (equivalent to half a gram of material) again determine the total reducing sugar by Allihn's method. Sucrose (see page 491) is obtained by multiplying the percentages of dextrose before and after inversion by the factor 1.044,⁵ then subtracting and multiplying

¹ U. S. Dept. Agr., Bureau of Chemistry, Bull. 1071 (revised), 241.

² THIS JOURNAL, 1, 299 (1909).

³ Where only total sugars after inversion are to be determined and the quantity of total sugars is small 8.8 grams are used and extracted in the usual way. Fifty cc. of the solution and 5 cc. of acid are inverted over night. The 55 cc. are neutralized with dry sodium carbonate and 25 cc. used for reduction. The figures obtained for dextrose represent the amount from 1 gram of material.

⁴ U. S. Dept. Agr., Bureau of Chemistry, Bull. 107 (revised), 49.

⁵ *Ibid.*, Bull. 107 (revised), 58.

the figure thus obtained by 0.95. No correction of the percentages obtained is necessary for the volume of the material, but when working with very wet material the results should be corrected for the dilution caused by the moisture content of the sample.

COMPARISON OF THE TWO METHODS.

The sodium carbonate digestion method having given good results on grains, the authors decided to test it in comparison with the alcohol method on various classes of material and to determine its limitations or the chance of error from differences in procedure. A number of representative samples were selected and comparative determinations made. The results obtained on samples of corn, wheat, and milo are given in the following table. The results in this table as in all tables are calculated to invert sugar.

RESULTS ON FEEDING STUFFS BY BOTH METHODS.

Serial No.	Substance.	Alcohol digestion method.		Sodium carbonate digestion method.	
		Reducing sugars.	Total sugars.	Reducing sugars.	Total sugars.
		Per cent.	Per cent.	Per cent.	Per cent.
7893	Corn.....	0.07	1.75	0.21	1.89
7917	Wheat.....	0.07	2.35	0.20	3.00
7916	Milo.....	0.15	1.38	0.25	1.43

These figures show that the two methods give results that are fairly comparable. In the case of the wheat, however, the sodium carbonate method gave results for total sugars that are a little higher than those obtained by the alcohol method. This, no doubt, is due to the fact that trouble was experienced in filtering the extract quickly and clearly after adding the alum, hence allowing the enzymes to become active again, a point which will be considered later in the discussion.

Samples of mixed cattle foods were then examined by the two methods, with the following results:

EXAMINATION OF MIXED CATTLE FOODS BY THE TWO METHODS.

Serial No.	Substance.	Alcohol digestion method.		Sodium carbonate digestion method.	
		Reducing sugars.	Total sugars.	Reducing sugars.	Total sugars.
		Per cent.	Per cent.	Per cent.	Per cent.
7856-A	Corn, cottonseed-meal, and alfalfa.....	0.00	2.99	0.42	3.30
7935	Corn, alfalfa ¹	0.09	0.26	0.43	0.26

It is to be noted that the sodium carbonate digestion method gives a perceptible quantity of reducing sugars, determined from the weight of the precipitated cuprous oxid. On examination of the cuprous oxid precipitate obtained in the sodium carbonate digestion method it was found that considerable organic matter was occluded in the precipitate, and also some mineral matter. This was traced back to the alum clarification, as alum does not clarify as completely as lead acetate. Using neutral lead acetate instead of alum for clarification in a second set of determinations on this material, the reducing sugar of the first sample came down to 0.00 and of the second sample to

¹ This sample had undergone fermentation.

0.08 per cent. With the lead clarification it is seen that the results compare more closely.

With other materials, such as molasses feeds and plants, high in nitrogenous bodies, when alum was used as a clarifying agent, it was noted that the precipitated cuprous oxid in the direct reducing-sugar determination was badly contaminated, a greenish flocculent mass occurring quite often. When neutral lead acetate was used no indication of this greenish precipitate was noted in the determination of reducing sugars in these samples. This shows alum to be a poor clarifying agent for sugar determinations by this method and indicates that neutral lead acetate should be used for this purpose. In no case, however, should lead subacetate be used as a clarifying agent, as its power of precipitating reducing sugars is well known.¹

As has been suggested, errors are likely to be introduced in the cuprous oxid weighing method by the presence of mineral salts and organic matter. Fehling's solution being strongly alkaline will cause in some cases a precipitation of salts on the introduction of the sugar solution. For this reason it is better to determine the copper in the precipitated cuprous oxid by some such method as Low's.² Burning the cuprous oxid to cupric oxid will only correct for the organic matter, so it could not replace an actual copper determination.

A comparison of these methods on samples of commercial feeding-stuffs, of which molasses was one of the ingredients, resulted as follows:

RESULTS ON MOLASSES FEEDS BY THE TWO METHODS.

Serial No.	Alcohol digestion method.		Sodium carbonate digestion method.			
			Lead acetate.		Alum clarification.	
	Reducing sugars. Per cent.	Total sugars. Per cent.	Reducing sugars. Per cent.	Total sugars. Per cent.	Reducing sugars. Per cent.	Total sugars. Per cent.
7894	3.55	7.90	4.54	8.68	5.98	9.07
7901	4.98	9.86	5.53	10.44	6.15	11.17
7900	2.54	28.82	3.25	32.15	3.41	32.37
7934	5.38	10.09	7.11	11.37	(³)	(³)
8049	1.81	33.65	1.88	34.36	(³)	(³)
8050	1.15	11.54	1.26	11.89	(³)	(³)

These figures show some peculiar variations. In the sodium carbonate digestion method when lead was used as the clarifying agent the results are lower and more closely approach the alcohol digestion figures. In samples No. 8049 and 8050 the results by the two methods are fairly comparable, but in the others, and especially in No. 7900, the sodium carbonate digestion method gives much higher figures for the percentage of total sugars, while in Nos. 7894, 7901, and 7934 the increase in total sugars is not so large as the increase in reducing sugars. The original samples left were not large enough to determine the cause of this increase. For sample No. 7900 the increase in total sugars amounts to 3.33 per cent. The results on this sample were carefully checked and the determination was also made by the section of plant physiological chemistry and the results as shown in the table agreed

with those obtained by the sugar laboratory. A portion of the sample was placed in a Soxhlet extractor and extracted with alcohol until no sugar was found in the alcohol by the *a*-naphthol test. Another portion of the sample was boiled for two and a half hours with a measured quantity of water and the sugar determined in this extract. Little or no starch was present in this sample, so that this method could be used. The results of this work are given in the following table:

CHECK ANALYSES OF SAMPLE NO. 7900 (MOLASSES FEED), USING SEVERAL METHODS.

Methods.	Reducing sugars. Per cent.	Total sugars. Per cent.
Alcohol digestion method ¹	2.54	28.82
Alcohol digestion method ²	2.81	28.98
Alcohol digestion method ³	3.10	29.54
Alcohol extraction (Soxhlet extractor) ⁴	2.75	29.24
Sodium carbonate digestion method ¹	3.41	32.36
Sodium carbonate digestion method ²	3.52	31.74
Sodium carbonate digestion method ³	3.28	32.11
Hot water digestion ³		32.44
Hot water digestion ²	2.94	31.68

The results obtained with alcohol, either by digestion or by extraction, agree among themselves, as do also the results with hot water and cold sodium carbonate digestion, but comparing the figures obtained when water was the extracting agent with those obtained when alcohol was used, there is noted an increase of over 3 per cent. in total sugars extracted by water. Unfortunately after this work was done none of the sample was left on which to study the cause of this difference. It might result (1) because the alcohol did not extract all the sugars; (2) because the sodium carbonate did not inhibit the action of the enzymes; (3) because the cuprous oxid was badly contaminated in the sodium carbonate digestion; (4) because the sodium carbonate method extracts substances which reduce Fehling's solution, especially on inversion, and that are not extracted by alcohol.

The first suggestion is answered by the fact that extraction in a Soxhlet extractor was run to a point at which no reaction for sugar with *a*-naphthol was given, and the results of this method were practically the same as those obtained by the alcohol digestion method. Also in experiments using 12 grams of sucrose as the material for extraction by the alcohol method in one test and 12 grams of invert sugar in another, there was no sugar remaining undissolved and no sugar was precipitated by the addition of 95 per cent. alcohol to the 300 cc. mark. This shows that the percentage of sucrose and invert sugar up to 100 per cent. would be soluble in the alcohol treatment. The second explanation was shown to be unsatisfactory by extracting the material with boiling water; the results obtained were practically the same as by the sodium carbonate extraction method in the cold and, therefore, the activity of enzymes could not have caused the difference.

¹ Results by Mr. Given.² Results by Mr. Straughn.³ Results by Mr. Jacobs.⁴ Results by Mr. Bryan.¹ Intern. Sugar Journal, 10, 602 (1908).² U. S. Dept. Agr., Bureau of Chemistry, Bull. 107 (revised), 241.³ No results by this method.

The third proposition is refuted by treating the crucibles coming from some of these determinations with nitric acid and determining the copper by Low's method.¹ Calculating this copper to invert sugar, the results were somewhat lower, but practically the same difference remained between the results by the two methods. Having eliminated the other possibilities the cause of the difficulty seems to narrow down to the nature of the substances extracted by the two solvents. Water removes from vegetable matter together with sugars many other substances, such as gums, pentosans, and some glucosids. These as a rule are more soluble in water than in 50 per cent. alcohol and some are rather easily hydrolyzed by acids, yielding reducing sugars. From the previous table it is seen that the principal increase occurs in the total sugars or in the sugars after inversion, and not so much so in the sugars before inversion. A new sample of this particular molasses feed (No. 8049, page 489) was obtained from the manufacturer with a view to studying this point further, but the results on this sample showed such slight differences by the two methods that no further work was deemed necessary. In the case of molasses feeds it is of extreme importance to have the sample finely ground before extraction. Especially is this so when using the alcohol digestion method, as the alcohol tends to hold back gummy material and this might coat the larger particles of the sample and keep them from being extracted. Molasses feeds are difficult to grind at the best, as they cake very readily, but by first drying carefully they can be finely ground.

Having compared the results obtained by the two methods on representative samples, it now remains to study the limitations of these methods.

LIMITATIONS OF THE METHODS.

Sodium Carbonate Digestion Method.

The purpose of the addition of sodium carbonate is to inhibit enzymes. Should the material under extraction be acid in reaction, then a portion or all of the sodium carbonate will be neutralized, and the necessary amount of sodium carbonate to inhibit enzymes will not be present. It was found that the acidity of one sample of molasses food neutralized about 90 per cent. of the sodium carbonate and in two others over 50 per cent. was neutralized. Therefore in using this method it is seen that the acidity of the material must be determined and corrected by the addition of more sodium carbonate, otherwise the results obtained would not be correct if the material contained active enzymes.

As the addition of alum or lead for clarification neutralizes the sodium carbonate, and therefore removes the agent inhibiting enzymic action, the procedure from this point must be hastened as much as possible to prevent changes in the sugar content. Should the filtration of the clarified solution be difficult and some time be consumed in obtaining a clear filtrate, it is better to throw away the solution and extract the sample again, as the results are very apt

to be incorrect. The few results in the following table will show the possible errors in such determinations:

RESULTS SHOWING ERRORS INTRODUCED BY SLOW FILTRATION.

Serial No.	Material.	Quick filtration.		Slow filtration and less speed.	
		Reducing sugars.	Total sugars.	Reducing sugars.	Total sugars.
		Per cent.	Per cent.	Per cent.	Per cent.
7959	Wheat.....	0.18	1.73	0.32	2.05
7959	Mixed cattle feed.....	1.50	4.03	1.63	5.06
7894	Molasses feed.....	5.98	9.07	6.77	10.40

The more time consumed from the point of clarifying to that of determining the reducing sugar, the greater will be the error. Determinations were made on the fresh extract and on the extract that had stood over night after clarification.

A few of the results are given in the following table:

DATA SHOWING EFFECT ON RESULTS OF STANDING OVER NIGHT.

Serial No.	Sample No.	Immediate determination.		Standing over night.	
		Reducing sugars.	Total sugars.	Reducing sugars.	Total sugars.
		Per cent.	Per cent.	Per cent.	Per cent.
7856-B	1	0.23	1.86	1.66	3.83
7856-C	2	0.38	2.42	1.72	2.22
7856-A	3	0.42	3.30	2.41	3.73
7893	4 Corn meal.....	0.17	1.98	1.23	2.25
7894	5 Molasses feed....	5.98	9.05	10.21	11.50
8207	Alfalfa.....	1.58	1.60	2.80	2.63
8209	Alfalfa and corn ¹ .	1.97	3.86	3.65	4.90

Standing over night in all cases greatly increased the reducing sugar content. In some instances this increase was over 500 per cent. The total sugars in all except one case (No. 7856-C) showed a marked increase, but the percentage increase is far below that of the reducing sugars. From the last two tables it is seen that allowing the solution to stand for any length of time after clarification increases the percentage of sugars present. This increase is due, no doubt, to enzymic action; the inhibiting agent having been neutralized, the enzymes again become active.

Time is an important factor in chemical analysis, as a chemist is often called away from his work and the solution in consequence stands for some time. It is well, therefore, to have a method that will allow of such delays without seriously affecting the results. When using the sodium carbonate digestion method such a lapse of time will certainly introduce an error, and it is readily seen that only the results which have been obtained by following very closely the procedure as outlined can be relied upon.

ALCOHOL DIGESTION METHOD.

The limitations of the sodium carbonate do not seem to apply in the case of the alcohol method. No substance need be added to the alcohol to destroy or inhibit the enzymes, as the alcohol itself and also the heat of extraction effects this. Hudson and Paine² have lately found that the enzyme invertase is de-

¹ U. S. Dept. Agr., Bureau of Chemistry, Bull. 107, (revised), 241.

² Lead acetate as a clarifier.

² U. S. Dept. Agr., Bureau of Chemistry, Circ. 58.

stroyed by 50 per cent. alcohol. After the enzymes are killed there is little chance of the extract changing on standing except through outside contamination. Church and Straughn¹ in their corn work have many times analyzed a portion of the fresh alcoholic extract and then shipped the remainder of their extract to be examined later. Results in all cases have been comparable, and the samples in some cases have been stored for from four to eight months before analysis. The alcohol method as given on page 487 indicates two or three points at which the work can be stopped and as much as a day or more elapse without fear of introducing any error. This is of great importance to the chemist who is called upon to make other determinations at the same time and who is liable to be called away from his work at any time. The natural acidity of the sample in this method does not play as important a part as in the other one. It is obvious, however, that if digestions of strongly acid substances are to be made the material should be neutralized. Again, if the alcohol used is strongly acid, it also should be neutralized.

DUPLICATING RESULTS.

Some methods will yield duplicate results when the determinations are carried on side by side that may not give concordant results when used at another time.

DUPLICATE ANALYSES MADE AT DIFFERENT TIMES BY THE SODIUM CARBONATE METHOD.

Serial No.	Number of analysis.	Reducing	Total
		sugars. Per cent.	sugars. Per cent.
7856-A	First.....	0.24	3.28
	Second.....	0.23	3.07
	Third.....	0.51	2.91
7856-B	First.....	0.23	1.86
	Second.....	0.38	1.94
7900	First.....	3.41	32.36
	Second.....	3.52	31.74
7934	First.....	7.11	11.37
	Second.....	6.57	11.46
8049	First.....	1.88	34.36
	Second.....	2.16	35.79
8207	First.....	1.40	1.48
	Second.....	1.58	1.60

The results by the alcohol method show possibly a little better agreement, as given in the following table:

DUPLICATE ANALYSES MADE AT DIFFERENT TIMES BY THE ALCOHOL METHOD.

Serial No.	Number of analysis.	Reducing	Total
		sugars. Per cent.	sugars. Per cent.
7856-A	First.....	0.00	2.99
	Second.....	0.00	2.93
	Third.....	0.00	3.00
7900	First.....	2.54	28.82
	Second.....	2.81	28.97
7934	First.....	5.72	10.12
	Second.....	5.82	10.47
8049	First.....	1.81	33.65
	Second.....	1.73	33.32
7959	First.....	1.46	3.91
	Second.....	1.57	3.99
	Third.....	1.55	4.15

¹ Bull. 127.

on the same sample. This is often noted when uncontrollable conditions which affect the results are present, or when the details of the manipulation are not accurately described in the method. When an extraction is to be made and the extract analyzed, questions of temperature and length of time of extraction are important. The latter point is generally taken into account by chemists, but temperature is not always considered unless special note is made of it. Directions to conduct extractions at room temperature are rather vague, for this temperature during the summer varies from that during the winter; and, again, some chemists prefer to work at a much lower temperature during the winter than others, and this plays an important part in the process. However, in the sodium carbonate method, the time, two and one-half hours, with occasional shaking, has been found long enough to remove the sugars under nearly all temperature conditions.

When using the greatest of care with the sodium carbonate method the results of determinations made at different times on the same sample seem to show a fair degree of agreement, as shown by the foregoing results.

TERMS USED IN STATING RESULTS.

As bearing on the general subject of sugar determinations, a word should be said regarding the methods of stating sugar results on such products as cattle feeds and grains. Some chemists calculate the reducing sugars to dextrose and some to invert sugar, while others state the reducing power in terms of metallic copper reduced by a given weight of the material under examination. The expression of the results in terms of sugars is more definite than in terms of copper reduction, which gives no clear idea of the amount present. Indeed, it is doubtful whether the reducing action noted is due to one particular sugar; it may be due to a mixture of several sugars or to invert sugar which is a mixture of equal parts of dextrose and levulose. In only a very few cases have the sugars been separated and identified. Therefore, for general work it seems that sugars before inversion should be reported as "reducing sugars calculated as dextrose" or "reducing sugars calculated as invert sugar," depending on which calculation was made. And for sugars after inversion the same phraseology should be used, namely, "total sugars calculated as dextrose" or "total sugars calculated as invert sugar." The increase in reducing sugars after inversion may not be caused entirely by the inversion of sucrose, but may be due to other compounds or sugars being split up into reducing sugars by the acid. It is well known that the ordinary inversion methods will hydrolyze other sugars, for instance, raffinose, and may hydrolyze such compounds as inulin or some of the glucosids and pentosans, forming reducing sugars. Under such circumstances it is certainly wrong to calculate the increase in reducing sugars as sucrose without a more definite knowledge of these sugars, although a part of this increase may be due to sucrose.

In order to eliminate a number of these compounds and restrict the increase to one or two sugars, the in-

vertase inversion method proposed by Hudson¹ should be used conjointly with the acid inversion. Under such circumstances, should the quantity of total sugars agree by both methods, one may safely say, with our present knowledge, that the increase in reducing sugars is due to sucrose, raffinose, or both. As the latter sugar is present in notable quantities in cottonseed-meal, and may be in other materials, it is not altogether safe to calculate this increase as sucrose with the idea that only sucrose is present. By the invertase method many other substances are eliminated. It seems better, therefore, to use the expressions (1) "reducing sugars calculated as dextrose," or "reducing sugars calculated as invert sugar;" (2) "total sugars by acid hydrolysis (or by invertase) calculated as dextrose," or "total sugars by acid hydrolysis (or by invertase) calculated as invert sugar," and (3) "increase in reducing sugars by acid hydrolysis (or by invertase) calculated as sucrose."

SUMMARY.

A method of preparing an extract for sugar determinations in grains, cattle foods, and vegetable material in general is given on page 487, depending on boiling the product with 50 per cent. alcohol. A comparison of the results obtained by this method using various classes of materials is given with that of a method depending on the extraction of the sugars with water at room temperature to which a percentage of sodium carbonate is added to inhibit enzymic action. A study of the limitations of the two methods is made, in which it is shown that the alcohol method will give satisfactory and comparable results on material, whether it is analyzed immediately or after standing for some time, while to obtain true and concordant results with the sodium carbonate method the most careful attention must be given to certain details of manipulation. In the sodium carbonate method, after neutralizing the sodium carbonate by clarifying with alum or lead, the work must be carried on with dispatch as the enzymes again become active; (2) the acidity of the sample must be determined and the quantity of sodium carbonate thereby regulated, or the accuracy of the results will probably be affected; (3) normal lead acetate should be used instead of alum for clarification under most circumstances, otherwise an error is introduced. Taking these points into consideration, it is the opinion of the authors that the alcohol method is to be preferred in general work, but when a long, comparable series of results is to be obtained on samples of the same kind of material the sodium carbonate method might be used advantageously, provided it is run with dispatch and the greatest care is exercised in its operation; and, most important of all, the results obtained by its use should compare with those obtained by alcohol digestion. Some materials, however, can not be analyzed by the sodium carbonate method because clear filtrations are not obtainable even with lead clarification.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No., 196.]

THE DETECTION OF SALICYLIC ACID.

By H. C. SHERMAN AND A. GROSS.

Received May 8, 1911.

For the detection of salicylic acid, especially when present in small amounts, it is customary in many laboratories to rely upon the violet reaction with ferric chloride, almost to the exclusion of other tests. The popularity of the ferric chloride test is readily explained by its simplicity and delicacy. Using fresh one per cent. ferric chloride as reagent the test is delicate in our hands to a dilution of about 1 : 400,000 when applied to 10 cc. of solution, about 1 : 750,000 to 1 : 1,000,000 if 25 cc. of solution be tested. The violet color obtained with such small amounts of salicylic acid must be observed quickly as it fades rapidly, passing through a rose-red color. A faint rose color may also be obtained on addition of ferric chloride to solutions containing salicylic acid in amounts too small to show violet reaction.

Unfortunately, however, the formation of a violet color with ferric chloride is a reaction by no means confined to salicylic acid. Mulliken's tables¹ include many colorless compounds which give more or less distinctly violet reactions with ferric chloride and some of these also resemble salicylic acid in solubilities. That this may lead to error in the testing of foods for salicylic acid has been pointed out by several writers.²

Among the tests for salicylic acid, other than the ferric chloride reaction, are the formation of the methyl ester or the nitro-compound, the reactions with bromine water and with Millon's reagent, and the Jorissen test.

The adoption by Mulliken of the methyl-ester and nitration tests for the identification of salicylic acid is sufficient evidence of their value for cases in which enough salicylic acid is involved to make them available; but these tests and also the test with bromine water seem not to be sufficiently delicate for the detection of very small amounts.

In tests with Millon's reagent it was found that heating for some time increases considerably the delicacy of the test. When two drops of Millon's reagent were added to the solution to be tested, shaken in a test-tube, and immersed in a boiling-water bath with a blank test for comparison there was developed in the course of 45 minutes' heating a delicate reddish or pink color even in the presence of only minute amounts of salicylic acid. With practice and with blank tests for comparison no difficulty was found in detecting the presence of 1 part salicylic acid in 2,000,000 of water when 20 cc. were tested; when only 10 cc. were tested, the pinkish tint was barely perceptible at this dilution. Longer heating and variations in the amount of reagent added were tried without appreciably altering the result. The limit of delicacy

¹ "The Identification of Pure Organic Compounds."

² Brand, *Ztschr. f. d. ges. Brauw.*, **15**, 303; *Ber.*, **27**, 806; Erich, *Der Bierbrauer*, **24**, 465; Munsche, *Woch. f. Brauerei*, **10**, 739; Abraham, *Journ. de Pharmacie de Liège*, **5**, 173; Backe, *Annales des Falsifications*, Nov., 1909; Sherman, *THIS JOURNAL*, **2**, 24; Backe, *Compt. rend.*, **150**, 540; **151**, 78.

of the test with Millon's reagent as here used seems, therefore, to be reached by heating in boiling water for 45 minutes and to lie at a dilution of about 1 : 2,000,000.

The Millon reaction also has the advantage over the ferric chloride test that the color produced even with very small amounts of salicylic acid shows no evidence of fading on standing over night; but on account of the large number of substances which respond to the Millon reagent¹ it seems unlikely that this reaction will prove as useful as that of Jorissen.

The Jorissen reaction² has been used by a number of European investigators³ for the identification of small amounts of salicylic acid and was found useful by one of us⁴ as a means of distinguishing between salicylic acid and maltol or isomaltol when present in small quantity in foods.

In further experiments with this reaction we have found that by diminishing the amount of copper used and increasing the time of heating, the test can be made much more delicate than appeared in our earlier work in which the test was used in its original form, and considerably more delicate than the ferric chloride reaction. The longer heating is necessary to fully develop the characteristic color, at least when only very small amounts of salicylic acid are present, and the reduction in the amount of copper diminishes the slight green color due to the reagent which otherwise may interfere with the more delicate tests.

The test as now used for very small amounts of salicylic acid is as follows: Bring the solution to be tested into a test tube, add 4-5 drops of 10 per cent. sodium or potassium nitrite, 4-5 drops of 50 per cent. acetic acid, and 1 drop of one per cent. copper sulphate. Shake after addition of each reagent and finally place in a boiling-water bath in such position that the test liquid is completely immersed in the boiling water and allow to stand for 45 minutes, then remove, allow to cool and examine against a white background, viewing the tube both vertically and horizontally and comparing with a blank test in which the same amounts of reagents have been added to pure water.

In this way, the presence of as little as 0.005 to 0.01 milligram of salicylic acid in pure water solution can be detected. Faint but perceptible reactions were obtained with 5 to 8 cc. of a solution of 1 : 1,000,000 and with 18 to 25 cc. of solutions of 1 : 3,000,000 to 1 : 3,500,000.

No advantage has been found in a brine-bath over a water-bath, in longer heating than 45 minutes, nor in varying the amounts of nitrite and acetic acid used. When larger amounts of salicylic acid are present a drop of stronger copper sulphate solution may be used,

¹ Vaubel, *Ztschr. angew. Chem.*, **1900**, 1125; Nasse, *Pflüger's Archiv. f. d. ges. Physiol.*, **83**, 361 (1901); Mann, "Physiological Histology," pp. 321-23, and "Chemistry of the Proteids," p. 7.

² Jorissen, *Bulletins de l'Académie Royal des Sciences, des Lettres, et des Beaux-arts de Belgique*, 3rd series, **3**, 259.

³ da Silva, *Compt. rend.*, **131**, 423; Klett, *Pharm. Centr.*, **41**, 452; *Ztschr. Unters. Nahr. Genussm.*, **4**, 469; Portes and Desmoulières, *Annal. chim. anal.*, **6**, 401; *Ztschr. Unters. Nahr. Genussm.*, **5**, 468; Windisch, *Ibid.*, **1**, 447.

⁴ Sherman, *THIS JOURNAL*, **2**, 24.

up to a ten per cent. solution as originally recommended. Except with very small amounts of salicylic acid the red color of the Jorissen reaction develops quickly on heating and the long immersion in the water-bath then becomes unnecessary if only qualitative results are required.

A feature which will be of great importance in colorimetric estimations of small amounts of salicylic acid is that while the violet color of the ferric chloride test fades rapidly, the red color of the Jorissen test is quite stable. Even the faint colors obtained by long heating, where only very minute amounts of salicylic acid are involved, have shown no deterioration when allowed to stand over night.

It has also been found that the ferric chloride and Jorissen tests may be applied to the same solution of salicylic acid. After making the ferric chloride test the liquid may be diluted until the violet color disappears and then submitted to the Jorissen reaction, when, if salicylic acid is present, pink color will appear.

No extended study seems to have been made to determine what other substances will give red or pink reactions in the Jorissen test. Jorissen, in describing his reaction, stated that phenol behaves in the same way as salicylic acid but benzoic acid does not. Allen states that neither benzoic, cinnamic nor tartaric acid responds to the Jorissen test, which statement we have confirmed.

Special importance attaches to the behavior in the Jorissen test of those substances which give violet reaction with ferric chloride. Maltol and isomaltol have already been considered; a few others have been tested with the following results:

Phenol, in our hands, gives the same color as salicylic acid in both the Millon and the Jorissen tests, but the limits of delicacy are quite different. Phenol can be detected by the Millon reaction to about 1 : 2,000,000. In the Jorissen test, phenol 1 : 100,000 gives practically the same color as salicylic acid 1 : 1,000,000.

Saligenin gives, in the Jorissen reaction, a red color at 1 : 10,000; a yellowish tint at 1 : 100,000; no reaction at 1 : 1,000,000. The limit of delicacy for the ferric chloride reaction with saligenin lies between 1 : 10,000 and 1 : 20,000.

2-oxy-isophthalic acid gives the Jorissen reaction up to a dilution of 1 : 100,000 but is easily distinguished from salicylic acid in the color which it gives with ferric chloride.

Methyl-ethyl-aceto-acetate, which gives, with ferric chloride, a violet-red color in concentrated solutions, gives neither the Millon nor the Jorissen reaction when tested at a dilution of 1 : 1,000.

Orcin, arbutin, resorcin and phlorizin, which give blue, violet, or red-violet reactions with ferric chloride do not respond to the Jorissen test.

THE PRESERVATION OF EGGS.

By R. BERGER.

Received March 27, 1911.

While the preservation of eggs on a commercial scale by the cold storage system is universally adopted,

this method, for obvious reasons, is not well adapted for the consumer or small producer. To meet the needs of the latter, many experiments have been made to discover a method by which the best results might be obtained, and as a result the conclusion has been reached that immersion of freshly laid eggs in silicate of soda solution is the most efficacious.¹

In recommending silicate of soda solution, the fact that brine, as well as solutions of other antiseptics are employed in preserving eggs for technical purposes, such as for tanneries, etc., has not been ignored. These latter solutions, however, do not keep the eggs palatable, as they penetrate and contaminate them. On the other hand, silicate of soda, because of its colloidal nature, does not penetrate the egg membrane, its characteristic action being to close the pores of the shell.

In order to substantiate this hypothesis, I have experimented with many different substances, colloids as well as crystalloids, and while I found that many colloids, such as starch, gelatine, tannic acid, gum arabic, albumen, silicic acid and norgine,² were not absorbed by the lime shell, other colloids, as well as some crystalloids, were thus absorbed, all of these absorbed substances having an alkaline reaction. Caustic soda solution, however, penetrates the eggs very readily, causing the albumen to coagulate in a very few days. Many eggs, when immersed in a 5 per cent. solution of caustic soda, cracked within the first 24 hours, owing to the rapidly increasing pressure, while the others, not thus affected, increased about 2.5 per cent. in weight within a week.

As the closing of the pores of the shell by the action of silicate of soda causes the eggs to crack, when exposed to heat, many tests have been made to ascertain the length of time in which this closing of the pores takes place, and it was found that a solution of 1 volume commercial silicate of soda, 40° Bé., and 15 or 20 volumes of water, will close the pores within three to seven days, lime water being fully as effective in this respect. Sodium aluminate and castile soap acted somewhat slower, a solution of 1 part of the former in 15 parts of water requiring from 2 to 3 weeks, and a 1 to 20 solution of the latter about a month. Other solutions which close the pores are those of bicarbonate, di-, and especially trisodium phosphate. A 3 per cent. solution of barium hydrate acted much slower than lime water, although the latter contains only about 0.14 per cent. hydrate of lime. The concentration is of great influence. For instance, if 1 volume of silicate of soda be diluted with 120 volumes of water, none of the eggs would crack within a period of fifteen days.

Various writers differ somewhat in their opinions as to the relative merits of different preservatives, and difference in the quality of silicate of soda has also been considered as the cause of some of the

¹ U. S. Dept. Agric., *Farmers' Bulletins* Nos. 103, 128, 273 and 287. "Das Hühnerei als Nahrungsmittel und die Konservierung der Eier," by Strauch, Bremen, 1897; "Les divers procédés de conservation des Oeufs," by R. Nourissé (Paris), 1907.

² E. Schmidt, "Zur Kenntnis der Norgine," *Chem. Ztg.*, 1910, p. 1149-1150.

variations in the results obtained. I have accordingly experimented with eggs in crystallized silicate of soda, or "alkasil," $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 9\text{H}_2\text{O}$,¹ and four grades of commercial silicate of soda (supplied by courtesy of The Grasselli Chemical Company), varying practically between the formulas $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ and $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$. I have furthermore added caustic soda, and also lime, to silicate of soda high in SiO_2 , in order to bring down the SiO_2 percentage, and no great difference was found in regard to the pore-sealing action of these different actions. However, the weights of the eggs increased in the crystallized silicate of soda, the increase ranging from 0.6 per cent. in one week to 2 per cent. in five weeks, and similar increase in weights of eggs results when the latter are immersed in commercial silicate of soda, in which the SiO_2 percentage has been decreased by the addition of caustic soda, or lime, to such an extent that only 3 molecules or less of SiO_2 are in combination with 2 molecules of Na_2O in the solution. Moreover, while the weights of a great number of eggs, preserved in silicate of soda, remained constant within very close limits, the increases in the weights of eggs preserved in lime water, and especially in silicate of soda with a low percentage of SiO_2 , varied considerably. Alkasil does not, of course, keep eggs palatable, but it is interesting to note that they can be preserved in a caustic soda solution, if sufficient silicate of soda be added to have at least 2 SiO_2 for 1 Na_2O in solution.

To form an opinion on the permeability of the shells of preserved eggs, I kept a number of the latter in the open air for several weeks, and found that they would still crack when boiled. After 6 months in the atmosphere, their average loss in weight was only 6 per cent. against nearly 20 per cent. on unpreserved eggs. (Vaslined eggs showed no loss.)

DIRECTIONS FOR PRESERVING EGGS IN SILICATE OF SODA.

1. Use clean receptacles of glass, earthenware, wood or of most any material, if same is paraffined inside, and can be sealed hermetically. I found 1/2 gallon screw cap glass jars, which will hold 14 or 15 eggs, most satisfactory, and in every way advisable.

2. Common silicate of soda, a sirup thick liquid of 40° Bé. or over, gives good results. It should be kept well sealed by paraffined or vaselined paper, pasteboard or cork stopper, or other cover impermeable to air and moisture, to prevent it from gelatinizing. Glass stoppered bottles, however, should not be used, as a little silicate may find its way to the ground neck, and it will then be impossible to remove the stopper later on, as silicate of soda will cement the stopper to the neck of the bottle.

3. The water should be pure, boiled water being preferable.

4. One part of silicate of soda to be very thoroughly mixed with 10 to 15 parts, or 1 part powdered silicate dissolved in 30 parts water, this solution to be well cooled before immersing the eggs therein.

¹ F. J. G. Beltzer, *Rev. gén. chim.*, 18, Oct., 1909.

5. The eggs must be clean, with strong, sound shells. They should be put into the preserving fluid, if possible, the same day they are laid, especially in summer. Unfertilized eggs are not likely to spoil, even if they are not so fresh. However, it is one of the strongest points of this preserving method that fertilized eggs will keep perfectly well, if the above precautions are taken. (Incubation is said to start on fresh, fertile eggs, if they are kept for about 24 hours at a temperature of at least 80° F., but if the proper incubating temperature—about 102.5° F.—is not reached soon and maintained, the egg germs will die and cause the eggs to decay.)

6. As soon as the eggs are packed in the preserving liquid, the receptacle is to be carefully sealed with a paraffined or vaselined paper or pasteboard, or with a screw cap or other reliable and tight cover. This is necessary not only to prevent water from volatilizing, which would finally expose the upper eggs to the atmosphere, but also to prevent the carbonic acid of the air from decomposing the silicate.

7. The eggs packed in the well sealed jars should be stored in a cool place, especially at first, that is, before the egg germs have lost their vitality. However, the temperature must not drop below the freezing point.

THE EFFECT OF THE ENVIRONMENT OF CARBONATED BEVERAGES ON BACTERIA.¹

By C. C. YOUNG AND N. P. SHERWOOD.

Received April 4, 1911.

There is a tradition among bottlers of carbonated soft drinks, founded as far as can be learned on very little experimental data, that the conditions under which "soft" drinks are prepared are toxic to all bacteria.²

The basis of this idea appears to be statements in the literature which state that carbon dioxide under pressure markedly reduces the number of bacteria in water and that *B. typhosus* and *B. coli* show a reduction of 90 per cent. in 24 hours when exposed to carbon dioxide under pressure. However, the experiments that were available were not carried out under bottlers' conditions. The conception held by the majority of manufacturers is that so long as the water is clear and sufficiently soft to carbonate well, no thought need be given to its sanitary quality, as the carbon dioxide under pressure will kill any living organism.

It was the object of this investigation to find whether or not any pathogenic organism could withstand the unfavorable environment of the bottled carbonated beverages a sufficient length of time to reach the consumer.

Investigations of trade conditions showed that, with the possible exception of ginger ale, most of the "pops" put on the market are consumed within ten days from the time of bottling. In fact during the summer months many instances were found where the goods

¹ Paper read before the Kansas City Section, Amer. Chem. Soc., March 23, 1911.

² Sulz, "A Treatise on Beverages," p. 67; Karl F. Kellerman, *Plant Bulletin*, 100, Part 8, page 7; "Sterilization of Water by Citric Acid," *Scientific American*, 98, 201, March 21, 1908.

go directly from under the bottling machine to the consumer.

The following experiments were carried out under trade conditions, with the one exception, however, that all conditions were intensified.

Pop bottles of 240 cc. capacity and ability to withstand 20 pounds' pressure were used. All bottles except the ones to be inoculated with *B. typhosus* were washed in the usual manner; the latter were washed, boiled for 30 minutes and cooled. Several sets of bottles giving different conditions of environment were inoculated. Three sets, of eight bottles each, were inoculated from 48-hour broth cultures of *B. typhosus*, *B. coli communis* and *B. prodigiosus*, respectively, each bottle receiving 1 cc. of its respective culture. Syrup known as bottlers' lemon had been previously added. Four bottles from each of the three sets were then filled, in the usual manner, with carbonated water at 18 pounds' pressure, at 10° C., and capped. The remaining four bottles in each of the three sets were filled, in the usual manner, with uncarbonated water and capped.

In the fourth and fifth sets no organism was used for inoculation, syrup was added to one but not to the other, and both were filled with carbonated water and capped. A sample of the water used in bottling was also taken. Samples from each set were plated out in the University laboratories 4, 28, 80 and 244 hours after the filling of the bottles. All bottles were kept at room temperature to correspond with normal conditions in trade. In plating, plain agar was used for *B. prodigiosus*, both plain and litmus-lactose agar for *B. coli*, and litmus-lactose agar for *B. typhosus*. Litmus-lactose agar was used to aid in identification of the last-named organisms. Plates of *B. prodigiosus* were incubated at room temperatures and those *B. coli* and *B. typhosus* at 37¹/₂° C. *B. prodigiosus* was identified by its characteristic red pigment. Presumptive and confirmatory tests were used for *B. coli*. Agglutination in the hanging drop and the Widal reaction were used in identifying *B. typhosus*. The mean results obtained are tabulated below:

TABLE I.

Duration of exposure before examination.	CARBONATED WATER USED				
	With syrup.			Without syrup.	
	<i>B. typhosus</i> , No. per cc.	<i>B. coli</i> , No. per cc.	<i>B. prodigiosus</i> , No. per cc.	Not inoculated, No. per cc.	Not inoculated, No. per cc.
0 hours	200,000	950,000	850,000	300	20
4 hours	25,000	250,000	800,000
28 hours	9,000	20,000	250,000
80 hours	1,200	1,300	150,000
244 hours	110	900	5,000	150	0

TABLE II.

Duration of exposure before examination.	UNCARBONATED WATER USED.				
	With syrup.			Without syrup.	
	<i>B. typhosus</i> , No. per cc.	<i>B. coli</i> , No. per cc.	<i>B. prodigiosus</i> , No. per cc.	Not inoculated, No. per cc.	Not inoculated, No. per cc.
0 hours	200,000	950,000	850,000	20	..
4 hours	200,000	950,000	850,000
28 hours	50,000	(**)	(**)
80 hours	6,000	100,000	(**)
244 hours	900	40,000	110,000	200	..

(**) Slipped.

From the above tables we may note the following facts and conclusions:

1. That the number of organisms outside of those introduced was extremely small.
2. That there was a decided reduction in number of the organisms introduced, owing to standing 244 hours uncarbonated.
3. That there was a very marked reduction in numbers of all three organisms introduced, and especially of *B. typhosus*, owing to conditions existing in the carbonated bottles.
4. That there was not a complete killing out of the organisms introduced, during the entire experiment.
5. That *B. prodigiosus* and *B. coli* seemed to be somewhat more hardy than *B. typhosus*.

Undoubtedly the longevity of *B. typhosus* depends in a great measure upon the virulence of the organism, and as the results above show that some of the organism will live longer than the beverage is normally on the market, the manufacturer should not depend upon the percentage of reduction caused by the carbon dioxide and other substances used.

From the observation that the most hardy individuals can resist these adverse conditions for a considerable length of time, the logical conclusion is that no water should be used in the manufacture of a carbonated drink, that is, in the least suspicious, and if a doubtful water is the only source of supply, this should be subjected to treatment by some method of sterilization with subsequent filtration through a trustworthy and efficient filter.

KANSAS UNIVERSITY WATER LABORATORIES.

THE COMPOSITION OF THE APPLE AS AFFECTED BY IRRIGATION.

By C. E. BRADLEY.

Received April 1, 1911.

Coöperating with the horticultural department of this Station in connection with their irrigation inves-

year, a summary of which is herewith given. The samples were selected from the Station experimental plats in the Willamette and Rogue river valleys and were taken at the proper stage for picking. Analyses were made as soon as possible after picking, usually within two or three days.

In preparing samples, the apples were peeled and cored and then run through a small meat grinder and the ground product placed in sealed jars. Samples for analyses were weighed out soon after grinding before juice and pulp separated.

Moisture was determined in a vacuum oven at 75-80° C. and 20-25 inches vacuum.

For sugars, 2¹/₂ times the normal weight of pulp was placed in a 250 cc. graduated flask, 10 cc. lead sub. acetate added, made up to 200 cc. with water, and the flask shaken for several hours in a shaking machine. This shaking was found necessary to completely remove the sugars from the pulp. The flask was then made to mark. Reducing sugars were determined in this solution by Allihn's method after removing lead with Na₂CO₃ and Na₂SO₄. Cane sugar was determined by the method of Clerget, the inversion being carried out in the cold according to official methods. For acid, 5-10 grams of pulp were weighed into a 200 cc. beaker, 100 cc. water added and the whole boiled for a few minutes, then titrated with N/10 NaOH, using phenolphthalein as indicator.

In the table of averages Nos. 1, 2, 4 and 5 represent results of checks made on the same orchard so that all conditions except moisture supply are uniform. It will be noted that the irrigated samples are somewhat higher in moisture and consequently lower in solids than samples from the dry checks. Also that the irrigated apples contain higher percentages of sugar based on dry material. Apples from irrigated plats were in general larger than those from the unirrigated. Individual apples from a given plat showed very little variation among themselves and results from single

AVERAGE COMPOSITION OF IRRIGATED AND UNIRRIGATED APPLES.

No.	Description.	Original.					Irrigated.					Acid as malic Per cent.	
		Solids. Per cent.	Red sugar. Per cent.	Cane sugar. Per cent.	Total sugar. Per cent.	Ash. Per cent.	Acid as malic. Per cent.	Dry Material.					
								Solids. Per cent.	Red sugar. Per cent.	Cane sugar. Per cent.	Total sugar. Per cent.		Ash. Per cent.
1	Newtowns.....	16.17	7.21	4.64	11.85	0.27	0.62	100.00	44.58	28.69	73.27	1.66	3.83
	Medford.....												
2	Spitzenburgs...	17.60	8.41	5.77	14.18	0.29	0.51	100.00	47.77	32.77	80.54	1.64	2.90
	Medford.....												
3	Newtowns.....	15.23	7.29	4.62	11.91	0.22	0.80	100.00	47.86	30.33	78.19	1.44	5.25
	Medford.....												
Non-irrigated.													
4	Newtowns.....	18.98	7.38	4.73	12.11	0.32	0.96	100.00	38.87	24.91	63.78	1.68	5.06
	Medford.....												
5	Spitzenburgs...	18.81	4.59	0.28	100.00	24.40	1.48
	Medford.....												
6	Newtowns.....	15.67	6.27	4.23	10.50	0.25	0.70	100.00	40.00	26.99	66.99	1.59	4.46
	Corvallis.....												
7	Spitzenburgs...	16.92	6.37	5.84	12.21	0.25	0.75	100.00	37.64	34.51	72.15	1.47	4.43
	Corvallis.....												

tigations a large number of analyses of apples have been carried out in this laboratory during the past

apples agreed well with those obtained from composite samples.

¹ Expert Testimony, Chicago Drainage Canal Case. *Water Supply Paper No. 194*; Whipple, *Engineering Record*, 1904, p. 746; Houston, *Fourth Report Royal Commission*, 3, 20-58 (1904).

The protein content of the peelings tested averaged 0.70 per cent. while that of the edible portion was

0.20 per cent. Only traces of starch were present in the samples tested.

Credit is due Mr. L. A. Bundy and Mr. B. Pilkington for the analytical work involved in these investigations.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPT. AGRICULTURE, BY PERMISSION OF THE SECRETARY.]

THE EFFECT OF LOW TEMPERATURES ON GROUND CHICKEN MEAT.¹

By H. W. HOUGHTON, PH.D.

Received April 26, 1911.

INTRODUCTION.

While low temperature, as a means of preserving food, was familiar to the early settlers in this country, and was extensively practiced by them, it is only within comparatively modern times that the possibilities of this addition to the conveniences of modern civilization have been fully developed.

The earliest and most primitive form of cold storage was that of mother earth herself. Ice, as a means of preservation, was unknown in Colonial days, and the early pioneer sought to preserve his food by placing it in a cave. Where natural facilities were lacking, artificial caves or cellars were resorted to.

It was not until the latter part of the eighteenth century that the more progressive husbandmen resorted to ice, cut from neighboring streams and ponds, as a means of refrigeration, and so slowly did the new method find favor that it was not until 1805 that the first large house was built for the storage of natural ice. From this time, however, the trade grew by leaps and bounds, reaching its largest proportion in the period between 1860-1870.

To-day the demand for ice has become so great that the natural product is not sufficient, and the yield of the lakes and streams is supplemented with ice frozen by mechanical means.

As ice became more commonly used, careful study was given to the best means of utilizing it. The earliest method, and that still used in shipping poultry, fish, and oysters, was to bring the ice in direct contact with the article to be preserved. A more modern device is that of a chilled chamber whereby the food is kept cold without touching the ice.

But while the methods of cold storage above outlined were adequate to meet the needs of individual families or small communities, they were not sufficient to supply the ever-growing demand for food preservation. To meet this demand mechanical refrigeration has been introduced. The use of ice on a large scale has been abandoned, and in its place the large storage rooms are cooled by the frozen surfaces of pipes containing brine or ammonia. These rooms are utilized for the storage of animal and plant products at various temperatures ranging from below 0° to 40° F. This modern method has been found greatly superior to the old system in that the tem-

perature can be controlled more readily and held at any desired point, while at the same time a drier atmosphere is produced.

The growing needs of our civilization, and the ever-increasing localization of the food-producing area has made refrigeration on a large scale a vitally important factor in the life of the people. The distances between the large manufacturing cities in the East and the centers of food production in the central and western parts of the country make the proper preservation of foodstuffs a matter of extreme importance to the nation.

In supplying this preservation the refrigeration plants and cars have proved of great benefit. The advantages obtainable, however, are frequently abused. The consumer is placed at the mercy of the merchant, for the latter many times purchases a large supply of perishable food at a low price and places it in cold storage until higher prices can be obtained. This is practiced particularly in the case of game, which is held in cold storage from one Christmas to the next in order that the merchant may derive a larger profit. Then if there occurs a rise of temperature, necessitating a rapid sale of foodstuffs, the merchant, rather than sacrifice his profit, again places his stock in cold storage, to be sold when an opportune time arrives, and this process may be repeated for years. Not only game, but likewise all other varieties of human food, derived from the animal kingdom, are similarly held for sufficient storage periods to allow the merchants to demand fancy prices for articles which were purchased by them when the market was oversupplied. Then again, the increase of the sale of ice cream is so great on holidays that a large quantity is reserved in cold storage from one to five weeks in advance to meet the enormous demand for the one day.

It is only natural, therefore, that with the growth of its benefits and abuses, careful studies have been made and accurate data have been compiled as to the effect of refrigeration on several of the most important articles of consumption.

The purpose of the present investigation is to study the chemical changes occurring in ground chicken meat when placed in cold storage at from -6° to +6° F., with and without the presence of carbon dioxide. The experiments covered a period of five months, samples being analyzed monthly throughout the time. The investigation includes the separation and detection of the common enzymes. No effort, however, has been made in these experiments to determine the effect of such refrigeration on the activity of these enzymes.

HISTORICAL.

In 1872 M. Tellier,¹ reported that meat stored at from -2° to +3° C. retained its fresh qualities.

In 1874 Bouley² experimented with Tellier's process of refrigeration and concluded that meat stored for two months at from -2° to +3° C. developed a peculiar fatty odor that affected the flavor; that desiccation and oxidation occurred in the exposed portion of the fat and meat frozen for several months;

¹A thesis submitted to the George Washington University for the degree of Doctor of Philosophy.

that there was produced a protein compound that did not exist in the muscular tissue during life; lastly, that while a small part of the albuminoids disappeared, there were formed leucomaines, lactic acid, and a trace of alcohol. Pogziale, and a little later, in 1889, a commission appointed by the French Minister of War confirmed Bouley's conclusions.

In 1892, Grassman³ observed no harmful change or any loss in nutritious food value in pork and beef due to storage at temperature of -2° to -4° C.

In 1897, Gautier⁴ reported from his investigation of mutton and beef, stored for from five to six months at below zero, a slight loss of moisture, accompanied by an increase of digestible albuminoid materials. An increase of peptone in the frozen meats indicated the presence of a trypsin-like ferment.

In 1900, Glage⁵ stated that the maturation of meat preserved in chilled rooms was due to the existence of certain bacteria in the rooms. He arrived at the conclusion that in many cases the flora of the meat was similar to that of milk and cheese and that these bacteria play a part in the maturation of meat.

In 1901, C. Mai⁶ claimed that by proper chilling treatment putrefactive changes could be prevented, but that the action of ferments or enzymes still continued to some extent and either directly or indirectly caused the changes which take place in the so-called ripening of meats.

In 1903, Müller⁷ reported that if the temperature of the cold storage room is 2° or 3° C. the maturation of meat due to ferments went on, but putrefaction was prevented. The reaction of the living muscle was neutral, but it became acid when the myosine coagulated and the hardening of the muscle appeared. Accompanying the disappearance of the muscular striations, there was produced an abundant formation of granulations.

König⁸ made a summary of analyses of chicken meat by Stützer, Moleschott, König, Kranch, Allen-

dorff, Atwater, and Wood. As mean percentage values for the flesh of chickens, König gives the following:

Water.....	72.22
Protein.....	21.33
Fat (by difference).....	4.55
Nitrogen-free extract.....	0.75
Ash.....	1.15

In 1906, Grindley⁹ reported that the general appearance of undrawn refrigerated poultry was similar to that of fresh fowl, except in one respect, namely, a characteristic flavor that was not due to putrefaction but perhaps, as Müller states, to the ripening of the meat.

At the same time Bird¹⁰ made a practical test with drawn and undrawn turkeys. He hung the fowls, during the month of February, in the open air and found that at the end of the first week the undrawn turkey was perfectly sound while the drawn one showed distinct signs of decay.

In 1908, Higley¹¹ reported that the edible portions of healthy poultry, either fresh or cold-stored at 5° C., contained no harmful bacteria, toxines, or ptomaines.

During the same year H. W. Wiley¹² and his co-workers made an extensive investigation of the effect of cold storage on eggs, quail, and chickens. In these experiments the chemical, microscopic, bacteriological, histological, and organoleptic examinations of eggs, quail, and chickens, stored six months or more, gave results which differed entirely from those obtained by the examination of the fresh materials. With the exception of the chemical analysis the results indicate very clearly that the changes in eggs, quail, and chickens are recognizable after about six months in storage. The chemical analyses are given in the following tables.

At the same time that Dr. Wiley and his associates made their preliminary report, Richardson¹³ read a paper on "The Criteria of the Deterioration of Flesh

PERCENTAGE COMPOSITION OF FRESH CHICKEN MUSCLE.

Number.	Sample.	Kind of meat.	Water.	Fat.	Ash	Protein (N×6.25).	Kreatin (N×3.11).	Total solids.	Sum of constituents determined.
66	Plymouth Rock broiler.....	Light	75.50	0.49	1.17	23.46	1.10	24.50	97.92
		Dark	71.75	2.40	1.21	21.40	0.827	28.25	101.33
67	Plymouth Rock young roaster or broiler....	Light	75.73	0.17	1.33	21.84	1.01	24.27	100.08
		Dark	75.86	1.38	1.49	21.07	0.64	24.14	100.44
73	Plymouth Rock roaster.....	Light	73.30	0.51	1.24	22.52	0.920	24.70	100.92
		Dark	74.48	2.88	1.18	20.69	0.743	25.52	99.97
78	Rhode Island Red roaster.....	Light	73.56	0.98	1.26	23.50	1.01	26.44	100.31
		Dark	73.02	2.99	1.35	23.13	0.64	26.99	101.13
86	Rhode Island Red large roaster.....	Light	75.01	0.53	1.21	21.95	1.02	24.99	99.13
		Dark	75.94	2.15	1.13	19.77	0.796	24.06	99.78

PERCENTAGE COMPOSITION OF COLD STORAGE CHICKEN MUSCLE.

Number.	Time of storage, Months.	Kind of meat.	Water.	Fat.	Ash	Protein (N×6.25).	Kreatin (N×3.11).	Total solids.	Sum of constituents determined.
84.....	14	Light	73.67	0.27	1.10	23.01	1.16	26.33	99.21
		Dark	72.16	1.93	1.27	23.16	0.852	27.85	99.37
85.....	14	Light	72.22	0.27	1.14	24.36	1.10	27.78	99.16
		Dark	70.09	2.85	1.25	24.55	0.877	29.91	99.61
69a.....	24	Light	74.43	0.40	0.95	23.00	0.836	25.57	99.61
		Dark	73.11	2.04	1.07	22.78	0.761	26.89	99.76
79.....	24	Light	72.60	0.83	1.06	25.10	0.569	27.40	100.15
		Dark	69.52	2.93	1.21	25.50	0.715	30.48	99.87
82.....	48	Light	71.42	0.48	1.39	24.78	0.945	28.58	99.01
		Dark	67.10	3.80	1.35	26.28	0.914	32.90	99.44
83.....	48	Light	65.87	0.19	1.48	26.91	1.41	34.13	95.86
		Dark	65.48	3.10	1.59	27.00	0.801	34.52	97.97

Food" in which the author laid special emphasis upon the value of the determination of ammoniacal nitrogen.

Toward the close of the year 1908, Richardson and Scherubel¹⁴ made a chemical investigation of fresh and frozen beef. The chemical analyses indicated no marked difference between the percentage of nitrogenous compounds in the cold water extract of fresh beef and of beef frozen 554 days.

A subsequent paper by the same authors¹⁵ considered the cold storage of beef at temperatures above freezing point. In this article it is shown that in the case of beef kept at from 2° to 4° C. the analysis of the cold water extract showed a gradual increase of total solids, total nitrogen, albumose, meat base nitrogen, ammonia, and acidity in direct proportion to the increasing age and decomposition.

In 1909, Emmett and Grindley¹⁶ investigated the effect of cold storage on beef and poultry stored 22 and 43 days. They concluded that the slight changes that occurred did not alter the nutritive value of the meat. Pennington¹⁷ included in her report on "Studies of Poultry from the Farm to the Consumer" a review of the scientific work done in the United States on this subject, a statement of the industrial application of refrigeration to the handling of dressed poultry and eggs, based on a careful study of existing conditions, and a very suggestive section on the application of the scientific data so far obtained to industrial uses.

The knowledge of chicken fat is at present rather unsatisfactory. In 1897 Amthor and Zink¹⁷ reported the following tables as the results of their observations on both fat and the free fatty acids:

Chicken fat, specific gravity.....	0.9241
Melting point.....	33.40° C.
Solidifying point.....	21.27° C.
Iodin number.....	66.7
Saponification number.....	193.5
Reichert number.....	1.0
Acetyl number.....	45.2
Acidity (fresh).....	1.2
Free fatty acids, specific gravity at 15° C.....	0.9283
Melting point.....	30.40° C.
Solidifying point.....	32.34° C.
Iodin number.....	64.6
Saponification number.....	200.8

In 1903, Zaitscheck¹⁸ analyzed the fat of two chickens, one of which had been fed on corn and the other on corn and milk. His results are as follows:

ANALYSIS OF FAT FROM CORN-FED AND MILK AND CORN-FED CHICKENS.

Determinations.	No. 1.	No. 2.
	Corn-fed.	Corn- and milk-fed.
Specific gravity at 30° C.....	0.9129	0.9153
Melting point.....	36.0° C.	38.5° C.
Solidifying point.....	17.4° C.	22.0° C.
Melting point, free fatty acids.....	37.0° C.	39.5° C.
Solidifying points of free fatty acids.....	34.5° C.	35.5° C.
Refraction at 40° C.....		
Saponification number.....	214.0	216.8
Non-volatile fatty acids.....	95.3	94.8
Iodin number of fat.....	70.6	57.6
Iodin number of fatty acids.....	54.4	45.4
Volatile fatty acids.....	0.88	0.88
Free fatty acid calculated as oleic.....	0.40	0.49

PLAN OF EXPERIMENT.

Thirty-six carefully selected and milk-fed Plymouth

Rock chickens were purchased from a reputable dealer who killed, picked and packed them with ice in my presence. After allowing the chickens to remain in contact with the ice six hours, the light and dark meat were separated from the skin, loose adipose tissue and bones, ground, and mixed by hand for fifteen minutes in order to obtain a uniform sample. The final mixture of each variety of chicken meat was divided into enough portions of 300 grams each to supply samples for the monthly investigations. Analyses of each variety were made immediately, while the remaining portions were placed in cold storage at a temperature varying from -6° to +6° F.

The analytical methods used in this investigation were selected after careful consideration of the literature. In each determination two or three results were obtained, the average figure being recorded. By the exercise of the utmost care and by close attention to the manipulation of the methods and the use of the very best obtainable apparatus, results have been secured from which, conclusions can be drawn as to the chemical changes taking place in ground chicken meat at low temperatures.

In the following tables a distinction is made between chicken fat and chicken meat fat. The chicken fat was prepared by pressing the adipose tissue of the viscera. The chicken meat fat was prepared by extracting the dried meat with anhydrous ether. After completely removing the ether at the lowest possible temperature, the residue was used for analysis. The following analytical methods were used:

PREPARATION OF SAMPLE FOR CHEMICAL EXAMINATION.

Separate the sample as completely as possible from the bones and loose adipose tissue and pass it rapidly and repeatedly through a sausage mill until a thorough mixture and complete maceration are obtained. The sample must be kept on ice to prevent decomposition, and all of the determinations should be begun as soon as possible after the sample is prepared.

The determination of moisture, ether extract, total nitrogen, total sulphur and phosphorus were made according to the methods given in *Bulletin 107*, Revised Bureau of Chemistry, U. S. Department of Agriculture.

DETERMINATION OF FREE AMMONIA.

Place 5 to 10 grams of the chicken meat in a distillation flask with 500 cc. of water and 10 grams of light calcined magnesium oxide. Then connect the flask with a condenser and distil three successive 150 cc. of the liquid into tenth-normal hydrochloric acid. Titrate the residual acid with twentieth-normal sodium hydroxide. Calculate free ammonia from the result of the total distillation.

ANALYSIS OF THE COLD WATER EXTRACT.

PREPARATION OF EXTRACT.

Weigh duplicates of 20 grams of the chicken meat into 600 cc. Erlenmeyer flasks and add about 100 cc. of water containing chloroform. Shake the mass for two hours, after which filter it into a 500-cc. volumetric flask through cheese-cloth and wring it out by hand. After rinsing the hand with water, tie the meat loosely

in the cheese-cloth and repeatedly wash with 50 cc. portions until the amount of the water-soluble solution is 2000 cc. Filter the solution and preserve it with chloroform, being careful always to use the same variety of filter paper. If not, the analysis will vary to such an extent that any comparison will not be correct. The first 500 cc. of extract contains 91 per cent. of the total water-soluble nitrogen and practically the entire amount of coagulable nitrogen.

ACIDITY.

Measure 100-cc. portions of the cold water extract into beakers and titrate against tenth-normal caustic soda, using phenolphthalein. Express the acidity as lactic acid.

TOTAL NITROGEN.¹⁹

Measure out duplicate samples of 100 cc. and determine the nitrogen by the modified Gunning method.

COAGULABLE NITROGEN.

Measure out duplicate samples of 100 cc. of the cold water extract into beakers, place on the steam bath, and evaporate to 25-cc. volumes. (As no change in the acidity of chicken meat occurred while in cold storage, the solutions were not made neutral.) Filter the coagulable nitrogen, wash it thoroughly, and determine the nitrogen in the residue on the filter paper by the modified Gunning method.

AMINO ACIDS.

Make up filtrates from the determinations of coagulable nitrogen to the same volumes and cool to 12° C. Add 50 cc. of a 24 per cent. tannic acid solution and 6 grams of salt. Keep these solutions at 12° C. for twelve hours with frequent shaking. Filter, allowing filter to drain thoroughly, and determine nitrogen in the filtrates by the modified Gunning method. Correction is made for the previously determined free ammoniacal nitrogen and the nitrogen contained in the amount of tannin salt solution used.

PROTEOSES AND PEPTONE.

Deduct from the total water-soluble nitrogen the sum of the coagulable nitrogen, amino acid, and free ammonia of the cold water extract.

FREE AMMONIA IN COLD WATER EXTRACT.²⁰

Measure 500 cc. of water-soluble solutions into a

1000-cc. round distilling flask, add 10 grams of magnesium oxid, and distil ammonia into 5 cc. of tenth-normal hydrochloric acid, and filtrate the residual acid with twentieth-normal sodium hydroxid.

WATER-SOLUBLE SOLIDS AND ASH.

Evaporate 100 cc. of cold water extract in platinum dishes to dryness at the temperature of boiling water, place in a water oven, dry to constant weight, and weigh. Char and extract with water, filter, and ignite filter and residue to white ash. Add filtered portion, evaporate to dryness, and ignite at a low temperature. The difference between the total water-soluble solids and the water-soluble ash will give the water-soluble organic matter.

VOLATILE SULPHUR COMPOUNDS²¹ (SULPHUR DIOXIDE, HYDROGEN SULPHIDE, HYDROSULPHIDE, THIO ESTERS.)

Weigh 25 grams of the meat into a beaker. After thoroughly mixing, place the contents of the beaker in a 1000-cc. round-bottom distilling flask, to which are added 500 cc. of water and 1 cc. of sirupy phosphoric acid. Connect the flask with a condenser which is so arranged as to collect the distillate in standardized alkali. After distilling over 300 cc. in a current of CO₂ (to prevent oxidation of the sulphur compound during distillation) determine the unneutralized standardized alkali. After adding bromine, evaporate the distillate to dryness and burn to a white ash. Dissolve residue in water, make slightly acid with hydrochloric acid and filter. After washing the filter paper thoroughly, determine the sulphates present as barium sulphate.

ANALYSIS OF FAT.

The determination of specific gravity, refractive index, iodine number, saponification number, soluble acids, Hohner number and free fatty acids are made according to methods in *Bulletin 107*, Revised, Bureau of Chemistry, U. S. Dept. of Agriculture.

PREPARATION OF FATTY ACIDS FROM FAT.²²

Saponify a quantity of fat by boiling 50 grams with 40 cc. of caustic potash solution (specific gravity 1.4), and 40 cc. of alcohol in a porcelain dish on a water bath with constant stirring until the soap be-

ANALYSES OF CHICKEN MEAT DURING A STORAGE PERIOD OF FIVE MONTHS.
LIGHT CHICKEN MEAT.

(All figures on basis of original meat.)

Length of storage. Days.	Mois- ture. Per cent.	Ash. Per cent.	Ether extract. Per cent.	Free ammoniacal		Total solids.		Organic ex- tractive. Per cent. (by difference).		Cold water extracts.		Amo- niacal nitro- gen. Per cent.	Acidity as lactic acid. Per cent.	
				Total nitro- gen. Per cent.	nitro- gen. Per cent.	Total solids. Per cent.	Ash. Per cent.	Total nitro- gen. Per cent.	Coagulable nitro- gen. Per cent.	Proteoses and peptone. Per cent.	Amino acid. Per cent.			
0	69.33	1.18	6.71	3.74	0.021	4.79	1.17	3.62	0.858	0.305	0.144	0.387	0.022	1.08
30	68.92	1.15	6.97	3.73	0.035	3.98	1.06	2.92	0.585	0.014	0.060	0.483	0.028	0.99
61	68.35	1.18	7.07	3.64	0.032	5.25	1.19	4.06	0.714	0.075	0.089	0.522	0.028	0.99
90	68.86	1.12	6.92	3.82	0.038	6.05	1.08	4.97	1.008	0.144	0.308	0.514	0.042	1.08
118	68.64	1.15	6.85	3.68	0.029	5.50	1.15	4.35	0.994	0.178	0.258	0.527	0.031	1.17
150	68.77	1.13	6.80	3.73	0.039	5.92	1.09	4.83	1.001	0.266	0.159	0.541	0.035	1.08
DARK CHICKEN MEAT.														
0	71.76	1.14	5.74	3.43	0.019	4.89	1.18	3.71	0.641	0.252	0.167	0.203	0.019	0.72
30	71.39	1.07	6.22	3.37	0.032	3.36	1.00	2.36	0.417	0.007	0.070	0.323	0.017	0.54
61	71.16	1.11	6.30	3.44	0.021	3.93	1.08	2.85	0.490	0.051	0.089	0.329	0.021	0.63
90	70.85	1.18	6.14	3.47	0.027	4.08	1.01	3.07	0.602	0.170	0.019	0.389	0.024	0.81
118	70.62	1.18	6.26	3.48	0.024	4.26	1.18	3.08	0.637	0.187	0.036	0.375	0.019	0.72
150	70.68	1.16	6.17	3.24	0.026	4.50	1.08	3.42	0.588	0.217	0.052	0.298	0.021	0.63

LIGHT CHICKEN MEAT.
(Calculated to moisture, ash and fat-free basis.)
Cold water extracts.

Length of storage. Days.	Total nitrogen. Per cent.	Ammoniacal nitrogen. Per cent.	Total solids. Per cent.	Organic extractives. Per cent.	Total nitrogen. Per cent.	Coagulable nitrogen. Per cent.	Proteoses and peptone. Per cent.	Amino acids. Per cent.	Ammoniacal nitrogen. Per cent.	Acidity as lactic acid. Per cent.
0	16.42	0.092	21.03	15.89	3.77	1.34	0.632	1.70	0.096	4.74
30	16.25	0.152	15.71	11.07	2.54	0.061	0.261	2.10	0.122	4.31
61	15.55	0.137	22.43	17.35	3.05	0.320	0.380	2.23	0.120	4.23
90	16.54	0.164	26.19	21.51	4.36	0.623	1.33	2.23	0.182	4.84
118	15.75	0.124	23.54	18.62	4.25	0.762	1.10	2.26	0.133	4.88
150	16.01	0.167	25.41	20.73	4.29	1.14	0.682	2.32	0.150	4.51

DARK CHICKEN MEAT.

0	16.06	0.089	22.81	17.37	3.00	1.18	0.782	0.950	0.089	3.37
30	15.81	0.150	15.77	12.43	1.96	0.033	0.328	1.52	0.080	2.53
61	16.05	0.098	18.34	13.30	2.29	0.238	0.415	1.54	0.098	2.94
90	15.89	0.124	18.69	14.06	2.76	0.779	0.087	1.78	0.110	3.71
118	15.85	0.109	19.42	14.04	2.90	0.852	0.255	1.71	0.086	3.19
150	14.73	0.118	20.46	15.55	2.67	0.987	0.236	1.36	0.095	2.86

comes pasty. Dissolve the soap in 1000 cc. of water, and boil the solution to evaporate the alcohol; this can be effected readily by replacing the water as it boils away. Next decompose the soap by means of dilute sulphuric acid. When by continued boiling the fatty acids have been obtained as a clear oily layer, free from solid particles, floating on the aqueous liquid, draw off the latter by means of a siphon and wash the fatty acids several times with hot distilled water until all the mineral acids have been removed. Since the fatty acids of lower molecular weight dissolve in hot water, and may redden litmus paper, methyl orange should be used to test for the complete removal of the mineral acid. Then place the dish containing the fatty acids on the water bath and

warm it until they are completely liquefied. The water and impurities will settle out and the warm acids may then be poured through a dry plaited filter fitted in a hot water funnel. The fatty acids will thus be obtained sufficiently dry for examination. If they solidify at the ordinary temperature, it is advisable to allow the fatty layer to solidify, then to perforate the cake by means of a glass rod, pour off the acid liquid, and wash with hot water as before.

REFRACTIVE INDEX AND IODIN ABSORPTION NUMBER OF CHICKEN MEAT FAT.

Length of storage. Days.	Refractive index at 40° C.	Iodin absorption number.
LIGHT.		
0	1.4660	39.92
30	1.4655	40.70
61	1.4660	44.58
90	1.4630	47.14
118	1.4615	52.23
150	1.4615	52.50
DARK.		
0	1.4680	40.74
30	1.4670	41.15
61	1.4685	42.11
90	1.4645	50.66
118	1.4635	53.80
150	1.4630	53.00

PER CENT. OF SULPHUR AS SO IN CHICKEN MEAT.

(Calculated to moisture-free basis.)

LIGHT CHICKEN MEAT.			
Length of storage. Days.	Total sulphur. Per cent.	Soluble sulphur. Per cent.	Volatile sulphur. Per cent.
0	2.67	0.489	0.000
30	2.57	0.485	0.009
61	2.40	0.348	0.028
90	2.67	0.546	0.022
118	2.77	0.604	0.019
150	2.82	0.576	0.022

DARK CHICKEN MEAT.

Days.	Per cent.	Per cent.	Per cent.
0	3.65	1.200	0.000
30	3.31	0.979	0.010
61	3.30	0.937	0.045
90	3.36	1.060	0.044
118	3.47	1.090	0.031
150	3.48	1.020	0.034

PER CENT. OF PHOSPHORUS AS P₂O₅ IN CHICKEN MEAT.

(Calculated to moisture-free basis.)

LIGHT CHICKEN MEAT.		
Length of storage. Days.	Total phosphorus. Per cent.	Soluble phosphorus. Per cent.
0	1.96	1.24
30	1.93	1.19
61	1.86	1.42
90	1.57
118	1.88	1.50
150	1.89	1.54

DARK CHICKEN MEAT.		
Days.	Per cent.	Per cent.
0	2.23	0.92
30	2.17	1.12
61	2.08	1.43
90	2.02	1.44
118	1.97	1.40
150	2.01	1.43

ANALYSIS OF CHICKEN FAT.

Determinations.	Exposed		
	Fresh.	two weeks to room temperature.	30 days in cold storage.
Specific gravity at 100° C.....	0.9002	0.8977	0.9013
Iodin number.....	59.77	58.48	59.80
Saponification number.....	193.30	196.75	193.47
Soluble acids as butyric acid...	0.38	1.67	0.40
Hehner number.....	88.52	91.20	87.00
Free fatty acids as oleic.....	0.247	2.47	0.269
Free fatty acids:			
Specific gravity at 100° C....	0.8659	0.8715	0.8670
Iodin number.....	56.74	53.60	57.02
Saponification number.....	216.52	214.25

DISCUSSION.

The samples of chicken meat when taken from the freezer presented a slightly dried appearance on the exposed surfaces but the moisture content of these samples as compared with that of the original meat is not perceptibly changed. The same is true of the ash, ether extract, acidity, and total nitrogen. However, this lack of variation does not apply to every result found, especially in the cases of the nitrogenous bodies of the cold water extract, for in meat, when it

undergoes ordinary deterioration from enzymic and bacterial processes, there is a conversion of insoluble proteins into soluble forms and of coagulable forms into non-coagulable by the continued hydrolytic splitting of large molecules into smaller ones with the final production of amino acids, acid amides, lower fatty acids and ammonia. As a natural assumption from these alterations in the composition of the meat at low temperatures, the organic extractives of the meat would increase and thereby cause a slight increase of water-soluble nitrogen. In order, however, to understand more clearly the exact changes that occur, the individual determinations must be discussed.

The total solids of the cold water extracts of both light and dark chicken meat decreased remarkably the first thirty days though this change was more noticeable in the dark meat. This decrease seems to be caused by the initial effect of the cold temperature on the original coagulable nitrogen which showed a greater decrease than any of the nitrogenous constituents determined. Mr. Müller⁷ states that cold temperature coagulated the myosine and increased the acidity of meat. This seems evident from the marked decrease of the total solids in the cold water extracts of the four samples of chicken meat of the same origin. The gradual increase of total nitrogen after thirty days, in both varieties of chicken meat, is probably caused by the action of bacteria and enzymes upon the meat, forming substances which are soluble in water. These deteriorating agencies appear to be more active in the light chicken meat than in the dark, or else the light meat is less resistant to the action than the dark meat, for in the former the total solids of the cold water extract reached a higher per cent. after 91 days in cold storage than those of the cold water extract of the original chicken meat, while in the latter case the total solids of the cold water extract increased gradually for 150 days, when it is slightly lower than that of the cold water extract of the original meat.

At the beginning of the experiments the organic extractives²³ of both the light and the dark chicken meat are the same, after which the results are parallel to the total solids of the cold water extracts. As this result was obtained by subtracting the water-soluble ash, which was practically constant throughout, from the total solids, there is no need of its discussion.

The total sulphur, soluble sulphur, and total phosphorus were constant. But this constancy does not hold true of the water-soluble phosphorus and volatile sulphur. There was a gradual increase of water-soluble phosphorus in both varieties of chicken meat during the first 90 days of cold storage, after which it remained practically constant. This increase, more noticeable in the dark chicken meat, can be traced back to the action of bacteria and enzymes on the phosphorus-containing, organic compounds of the chicken meat. There is a similar increase in connection with the cold storage of eggs, in which Cook²⁴ found an increase of inorganic phosphorus with a corresponding decrease of organic phosphorus. The

volatile sulphur increased slightly with the length of time in cold storage; these changes can be considered as a significant indication that both varieties of chicken meat had deteriorated.

The increase of free ammonia in the light chicken meat signifies that that variety of meat deteriorated to a greater extent than the dark chicken meat, in which the free ammonia is practically constant. This increase of free ammonia in storage chickens has been obtained by Pennington and Greenlee²⁵ in their application of Folin's method and by Weber and Houghton²⁶ in their investigations of the incipient deterioration occurring in chickens stored six months. Like the organic extractives, the total nitrogen of the cold water extract of both varieties of chicken meat decreased during the first thirty days, followed by a gradual increase. The increase of the total nitrogen in the cold water extract of the light chicken meat is so rapid that after ninety days in cold storage a higher per cent. is observed than on the original sample. This increase of water-soluble nitrogen seems to be characteristic of light meat. It has been shown that the total nitrogen of the cold water extract of quail²⁷ preserved in cold storage increased with the time of storage, while in the water-soluble nitrogen of the meat of the entire chicken, in which the dark meat predominates, a slight decrease was indicated. As the majority of the meat of quail is light, the increase of water-soluble nitrogen in the light chicken meat here studied is confirmed. Chittenden and Cummins²⁸ observed that the light chicken meat was more digestible than the dark. Although there was a gradual increase of the total nitrogen in the cold water extract of the dark chicken meat after the first thirty days, nevertheless after 150 days the total water-soluble nitrogen was slightly less than that of the original sample. Richardson²⁴ has found that the total nitrogen in the cold water extract of beef, which is dark meat, does not change after the meat has been in cold storage 554 days.

The coagulable nitrogen runs directly parallel with the organic extractives, total solids, and nitrogen of the cold water extracts. The decrease of coagulable nitrogen of each variety of chicken meat, which occurred during the first thirty days, verifies further the fact that myosine is coagulated by the cold temperature. The gradual increase of coagulable nitrogen in both light and dark chicken meat after the first thirty days is probably caused by the action of bacteria and enzymes on the protein material of the chicken while in cold storage, forming new nitrogenous bodies which are coagulable.

The increase of proteoses and peptone in the light chicken meat is the result of the deterioration which this variety of meat has undergone, as has already been discussed. With the dark chicken meat there was a slight decrease of proteoses and peptones. The increase of amino acids in both varieties of chicken meat can be traced to the maturation of the meat. The free ammonia of the cold water extract is practically identical with the free ammonia of the meat itself.

The analyses of the chicken fat indicate no change during thirty days in storage.

The iodine number of the chicken meat fat increases regularly for both varieties of meat.

CARBON DIOXIDE AS A PRESERVATIVE OF ANIMAL FOOD.

So slight is the literature on this valuable factor in the solution of the proper preservation of perishable food, that the discussion can hardly be considered as being in more than a tentative stage. Prof. Gamgee,²⁸ the originator of the means of preserving perishable food, found that meat, contained in vessels in which the entire amount of air had been displaced by carbon dioxide, was preserved for given periods. The exact preserving efficiency of carbon dioxide was not investigated until recently. Frankel,³¹ Altana²⁹ and Bruschettini³⁰ experimented on the effect of carbon dioxide on organisms, drawing the conclusions that the action of strict anaerobic and of

certain mixed aerobic bacteria was prevented and that of other forms was retarded by this gas.

In this investigation the chicken meat was placed in an air-tight desiccator having an inlet and outlet tube through which the carbon dioxide could be permitted to flow into the desiccators in such a manner as to displace the entire quantity of contained air and not injure the cell body of the meat. The carbon dioxide was allowed to flow slowly into the desiccator for fifteen minutes. In order to thoroughly investigate this mode of preserving meat in direct comparison with the present study of the effect of cold storage on chicken meat, portions of the same light and dark chicken meat used in the experimental work just described were placed in five desiccators filled with carbon dioxide, thereby affording samples for complete monthly analyses. These desiccators were placed in a chill room (0° C.) after the first month, as the temperature of the refrigerator (12°-13° C.) was not constant. Using the methods previously stated, the following results were obtained:

ANALYSES OF CHICKEN MEAT COLD-STORED, USING CARBON DIOXIDE.

LIGHT CHICKEN MEAT.

(All figures on basis of original meat.)

Length of storage. Days.	Moisture. Per cent.	Ash. Per cent.	Ether extract. Per cent.	Total nitrogen.		Total solids. Per cent.	Ash. Per cent.	Organic extractives. Per cent.	Total nitrogen. Per cent.	Coagulable nitrogen. Per cent.	Proteose and peptones. Per cent.	Amino acids. Per cent.	Ammoniacal nitrogen. Per cent.	Acidity as lactic acid. Per cent.
				Per cent.	Per cent.									
0	69.33	1.18	6.71	3.74	0.021	4.79	1.17	3.62	0.858	0.305	0.144	0.387	0.022	1.08
30 ¹	68.72	1.11	6.48	5.68	0.042	4.38	1.13	3.25	0.758	0.023	0.170	0.530	0.035	1.35
61	68.45	1.12	6.25	3.74	0.049	5.08	1.11	3.97	0.885	0.046	0.202	0.595	0.042	1.26
90	68.40	1.16	6.55	3.80	0.044	6.05	1.16	4.89	0.924	0.156	0.131	0.595	0.042	1.39
118	68.69	1.11	6.73	3.76	0.036	5.80	1.08	4.72	0.980	0.252	0.161	0.530	0.037	1.26
150	67.32	1.13	6.65	3.72	0.052	5.92	1.09	4.83	1.008	0.243	0.128	0.602	0.035	1.26

DARK CHICKEN MEAT.

0	71.76	1.14	5.74	3.43	0.019	4.89	1.18	3.71	0.641	0.252	0.167	0.203	0.019	0.72
30 ¹	71.61	1.11	5.68	3.39	0.030	3.76	1.18	2.58	0.553	0.014	0.105	0.406	0.028	0.67
61	71.56	1.16	5.70	3.33	0.032	3.88	1.09	2.79	0.630	0.091	0.115	0.403	0.021	0.72
90	70.88	1.19	5.99	3.54	0.034	4.25	1.08	3.17	0.633	0.163	0.115	0.327	0.028	0.85
118	71.22	1.16	5.97	3.51	0.031	4.26	1.12	3.14	0.613	0.191	0.030	0.363	0.029	0.81
150	71.51	1.15	5.76	3.47	0.033	4.37	1.10	3.27	0.630	0.207	0.057	0.338	0.028	0.72

NITROGENOUS CONSTITUENTS OF CHICKEN MEAT COLD-STORED, USING CARBON DIOXIDE.

LIGHT CHICKEN MEAT.

(Calculated to moisture, ash, and fat-free basis.)

Cold water extracts.

Length of average. Days.	Total nitrogen. Per cent.	Ammoniacal nitrogen. Per cent.	Total solids. Per cent.	Organic extractives. Per cent.	Total nitrogen. Per cent.	Coagulable nitrogen. Per cent.	Proteoses and peptone. Per cent.	Amino acids. Per cent.	Ammoniacal nitrogen. Per cent.	Acidity as lactic acid. Per cent.
0	16.42	0.092	21.03	15.89	3.77	1.34	0.632	1.70	0.096	4.74
30 ¹	15.58	0.177	18.49	13.72	3.20	0.097	0.718	2.24	0.148	5.70
61	15.47	0.203	21.01	16.42	3.66	0.190	0.835	2.46	0.174	5.21
90	15.91	0.184	25.32	20.47	3.87	0.653	0.548	2.49	0.176	5.82
118	16.02	0.153	24.71	20.11	4.17	1.07	0.686	2.26	0.158	5.37
150	14.94	0.209	23.77	19.40	4.05	0.976	0.514	2.42	0.141	5.06

DARK CHICKEN MEAT.

0	16.06	0.089	22.89	17.37	3.00	1.18	0.782	0.950	0.089	3.37
30 ¹	15.70	0.139	17.41	11.95	2.56	0.065	0.486	1.88	0.130	3.10
61	15.43	0.148	17.98	12.93	2.92	0.422	0.533	1.87	0.097	3.34
90	16.13	0.155	19.37	14.45	2.88	0.743	0.523	1.49	0.128	3.87
118	16.21	0.143	19.68	14.50	2.83	0.882	0.139	1.68	0.134	3.74
150	16.08	0.153	20.25	15.15	2.92	0.959	0.264	1.57	0.130	3.33

¹ In refrigerator at 12° C.; remainder of experiment conducted in chill room at 0° C.

PER CENT. OF SULPHUR AS SO₄ IN CHICKEN MEAT COLD-STORED, USING CARBON DIOXIDE.

(Calculated to moisture-free basis.)

LIGHT CHICKEN MEAT.

Length of time stored.	Total sulphur.	Soluble sulphur.	Volatile sulphur.
Days.	Per cent.	Per cent.	Per cent.
0	2.67	0.489	...
30 ¹	2.49	0.416	0.013
61	2.54	0.444	0.038
90	2.34	0.570	0.031
118	...	0.639	0.025
150	2.45	0.520	0.027

DARK CHICKEN MEAT.

0	3.65	1.20	...
30 ¹	...	1.16	0.017
61	3.34	1.02	0.028
90	3.37	1.10	0.044
118	3.61	1.09	0.031
150	3.59	1.08	0.031

PER CENT. OF PHOSPHORUS AS P₂O₅ IN CHICKEN MEAT COLD-STORED, USING CARBON DIOXIDE.

(Calculated to moisture-free basis.)

LIGHT CHICKEN MEAT

Length of storage.	Total phosphorus.	Soluble phosphorus.
Days.	Per cent.	Per cent.
0	1.96	1.24
30 ¹	2.01	1.34
61	1.88	1.49
90	...	1.52
118	1.89	1.47
150	1.90	1.47

DARK CHICKEN MEAT.

0	2.23	0.92
30 ¹	2.22	1.23
61	2.14	1.48
90	2.06	1.48
118	2.19	1.39
150	2.21	1.47

REFRACTIVE INDEX AND IODIN ABSORPTION NUMBER OF CHICKEN MEAT FAT COLD-STORED, USING CARBON DIOXIDE.

Length of storage.	Refractive index		Iodin absorption number.
	at 40° C.		
Days.	Light.		
..	1.4660		39.92
30 ¹	1.4645		49.08
61	1.4660		45.78
90	1.4615		47.38
118	1.4610		47.92
150	1.4610		48.05
	DARK.		
0	1.4680		40.74
30 ¹	1.4680		53.33
61	1.5685		52.00
90	1.4650		53.79
118	1.4630		53.03
150	1.4635		53.50

DISCUSSION.

The results of the experiments with carbon dioxide are so nearly identical with those obtained on the effect of low temperatures on chicken meat that it will be needless to enter into a discussion of them. There are, however, a few figures that verify the usefulness of carbon dioxide as a preservative of perishable foods.

The retarded increase of total water-soluble nitrogen of the cold water extract, accompanied by a rapid increase of proteoses, peptone and amino acids, is important in illustrating the inhibitory action of carbon dioxide upon bacteria.

If it is true that carbon dioxide has a retarding effect on the bacterial action in chicken meat, the

¹ In refrigerator at 12° C.; remainder of experiment conducted in chill room at 0° C.

changes that have occurred must be due to enzymes. However, to assure success in this method of employing carbon dioxide as a preservative of meat in refrigeration, there are three factors necessary: air-tight containers, complete displacement of the air without injuring the cell body of the meat, and a constant temperature below 12° C.

IDENTIFICATION OF ENZYMES IN GROUND CHICKEN MEAT.

Owing to the influence of the enzymic activity in animal tissue subjected to cold storage, it will be of interest to cite the investigations that have been recently made to identify the various enzymes present in animal tissues. The investigators who have contributed to the literature on this subject are Battelli, Frederic and Stein,^{32,33} Lob³⁴ and Mulzer,³⁵ Ville and Moitessier,³⁶ Kastle and Loevenhart,³⁷ Loew,³⁸ Bach,³⁹ Euler,⁴⁰ Shaffer⁴¹, van Itallie,⁴² Lesser,⁴³ Jolbauer and Zeller,⁴⁴ Ostwald,⁴⁵ Lockemann, Thies and Wichern,⁴⁶ Battelli and Stern,⁴⁷ Roaf,⁴⁸ Heffler,⁴⁹ Wakeman,⁵⁰ McCallum and Hart,⁵¹ Abelous and Gerard,⁵² Oppenheimer,⁵⁴ and Ranson.⁵⁵

The enzymes that have been detected in animal tissue are oxydase, peroxydase, catalase, protase, invertase, hydrolytic, nitrate reducing, phytin splitting, and glycolytic enzymes.

Each time the ground chicken was analyzed in the experiments just cited, an extract for the detection of enzymes was prepared. It was necessary to composite these residues since the extracts each month from the amounts of chicken that could be spared were insufficient to allow the tests to be made, in separating and detecting the enzymes the following methods were used:

PREPARATION OF EXTRACT FOR DETECTION OF ENZYMES.

The extract was prepared by extracting some of the finely ground meat several times with water saturated with chloroform. This extract was filtered and sufficient alcohol added to the filtrate to make a 60 per cent. solution. The liquid was shaken for half an hour and set aside for twenty-four hours, at which time an abundant flocculent precipitate had collected in the precipitating jar. The clear liquid was then siphoned off, the residue dissolved in water, and a solution of sodium phosphate and calcium chloride added until a heavy precipitate of calcium phosphate formed. This was allowed to settle, chloroform being added to prevent bacterial action. The clear liquid was again drawn off and the residue shaken up with water and filtered; this filtrate was dialyzed for twenty-four hours in running water; sufficient alcohol was then added to make an 80 per cent. solution and the mixture shaken violently for half an hour. The precipitate was allowed to settle for twelve hours and then filtered off, the precipitate being washed with 95 per cent. alcohol and dried. The powder thus obtained was of a light-brown color, soluble in water. The water solution of this powder was tested for enzymes as follows:

Oxydase.—To 5 cc. of a 5 per cent. solution of gum guaiacum in alcohol was added, drop by drop, the

solution to be tested, a boiled portion of the solution to be tested for enzymes being used as a check. No blue color was given by either the heated or unheated showing the absence of oxydase.

Peroxydase.—To 5 cc. of a gum guaiacum solution a few drops of hydrogen peroxide were added and then, drop by drop, the solution to be tested. Both kinds of meat gave a deep blue color, indicating the presence of peroxydase, while some of the boiled solution, when added to guaiacum extract, gave a brownish color, showing that peroxydase had been destroyed by boiling.

Protase.—A 10 per cent. solution of gelatin was prepared, thymol being added to prevent the interference of bacteria, and the solution was rendered slightly opaque by the addition of calcium carbonate. This was distributed in sterile tubes, approximately 5 cc. in each tube, and cooled rapidly to prevent the calcium carbonate from settling. Five cc. of 0.5 per cent. meat enzyme solution, containing a few drops of toluol, were added to gelatin tubes and these tubes set aside at room temperature for 24 hours. The gelatin was acted upon to some extent. In the check, which contained some of the boiled enzyme solution, the amount of gelatin remained constant.

Upon acidifying a portion of the enzyme solution, so that it contain 0.20 per cent. of HCl, and by making another portion alkaline with sodium carbonate and then testing the action of these solutions on gelatin tubes, the alkaline solution becomes more active. These results indicate an enzyme similar to trypsin.

Invertase.—Ten cc. of 10 per cent. cane sugar solution were added to 5 cc. of 0.5 per cent. enzyme solution, some toluol added, and the solution examined with a polariscope, then set aside at 38.5° C. for 12 hours and again tested with the polariscope, which showed the presence of invertase.

Lipase.—To 10 cc. of ethyl butyrate solution were added 5 cc. of meat enzyme solution containing some toluol; this mixture was set aside at 38.5° C. for 12 hours and the acidity determined, using phenolphthalein as indicator. The acidity was not increased.

Diastase.—Five cc. of a 0.5 per cent. of meat enzyme solution were added to a 1 per cent. starch solution, toluol added, and the mixture set aside in an incubator at 38.5° C. for 24 hours. The solution was then tested for reducing sugars by heating with Fehling's solution. There was no reduction in either case.

Catalase.—To 40 cc. of a solution of meat enzyme, containing 5 grams of enzyme powder to 100 cc. of water, 5 cc. of hydrogen peroxide solution were added and the amount of oxygen given off was measured. In thirty minutes a measurable amount of oxygen was given off. The check, which was a boiled solution of the enzyme, gave no oxygen when treated with hydrogen peroxide. This indicates that the enzyme solution has the properties of catalase.

*Nitrate-reducing Enzym.*⁵⁰—One-tenth of a gram of the enzyme powder was mixed with 25 cc. of a 1 per cent. potassium nitrate solution and set aside at

35° C. for two hours. Test clear solution with naphthalene hydrochloride solution and sulphonilic acid solution as given in Mason's "Water Analysis." A pink color indicated nitrites reduced by enzyme.

GENERAL CONCLUSIONS.

Chicken meat subjected to cold storage, even for a period of five months, showed certain physical and chemical changes which clearly demonstrated that it is not identical with fresh material.

The cold storage meat felt soft in marked contact to the firmness of the fresh chicken meat, and a slight characteristic odor was detected.

The chemical changes that apparently take place in the cold-stored meat by direct comparison with the original chicken meat are: (1) slight variations of moisture and ether extract; (2) a small increase of ammonia, especially in the case of the light chicken meat; (3) a decided increase of water-soluble nitrogen, total solids, and organic extractives in the light chicken meat, with a slight decrease of the same constituents in the dark meat; (4) a decrease of coagulable nitrogen in both varieties of chicken meat during the first thirty days, followed by a rise which did not reach that of the fresh sample; (5) an increase of amino acids in both kinds of chicken meat with an increase and decrease of the proteoses and peptones respectively in the light and dark chicken meat.

An increase of soluble phosphorus was indicated during the first 90 days of the storage period, which was more marked in the dark meat than in the light meat. In the cold-stored samples a little volatile sulphur was found, none being detected in the fresh meat. The analyses of chicken fat indicated a fairly constant composition, but in the chicken meat fat of the cold-stored chicken the iodine number increased regularly while the index of refraction decreased slightly.

The alteration particularly noticed in the light meat was inhibited to a certain extent by storing in an atmosphere of carbon dioxide, accompanied by an increased production of proteoses, peptones, and amino acids. The initial increased production of these nitrogen bodies is probably due to enzymic action during the first 30 days at 12° C.

The enzymes detected were peroxydase, catalase, protase similar to trypsin, invertase, and a nitrate-reducing enzyme.

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PLANTS AND MACHINERY.

AN ELECTRICALLY CONTROLLED CONSTANT TEMPERATURE WATER BATH FOR THE IMMERSION REFRACTOMETER.

By H. C. GORE.

The water bath of the immersion refractometer must be held within narrow limits at 17.5°C .—a temperature usually below that of the room. It is therefore cooled by the addition of cold water. Admitting tap water or ice water at a constant rate is unsatisfactory, as constant adjustment is required by changes in room temperature. The device herein described, by which water is added to the bath automatically, has given satisfaction during a period of

many months. No claim to originality can be made, in view of the many devices of this kind which have been proposed.

The tap water runs through the sight tube A (Fig. 1) and is diverted to the bath when the rubber tube B is closed by the lever of the sounder C. In warm weather the water is cooled by passing it through the copper coil D, immersed in ice water in the vessel E. The refractometer bath F is provided with an overflow pipe, K, and is stirred by a current of air entering through a tube not shown; E and F are insulated by magnesia packing to prevent the condensation of moisture which occurs during warm humid weather.

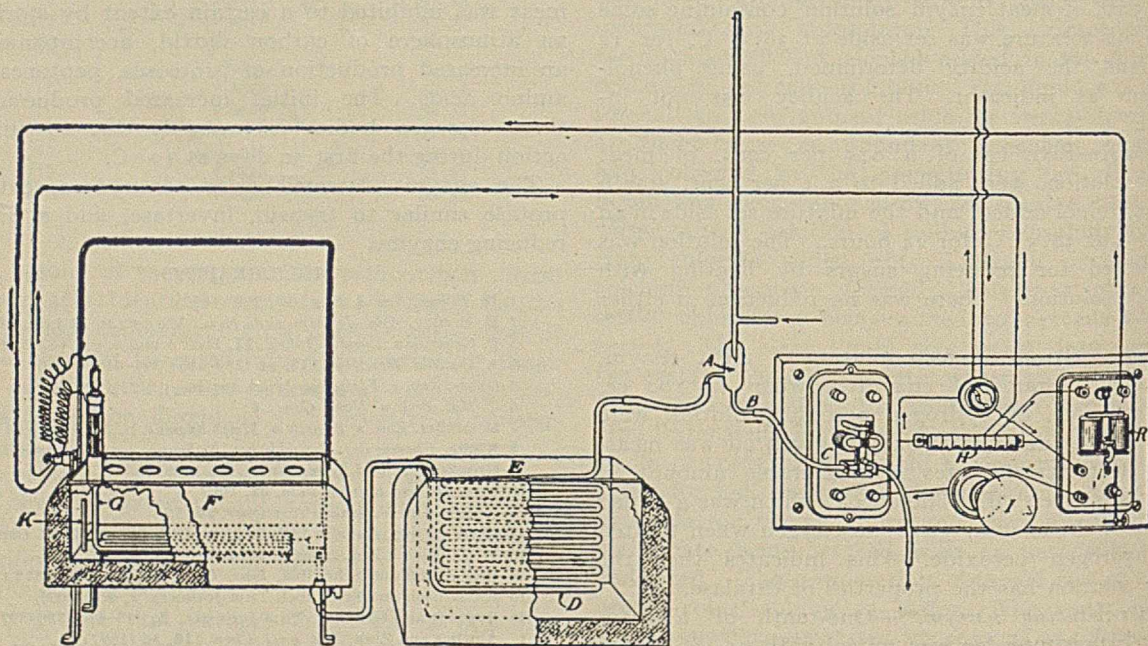


Fig. 1.

The thermostat G consists of a long glass tube bent into a flat rectangular coil and fastened to a perforated brass plate resting on short legs on the bottom of the bath. It is filled with mercury and closed at one end. To the open end is sealed a device shown in detail in Fig. 2. Electric connection is made with the mercury in the thermostat through the platinum wire A (Fig. 2) which passes through the glass wall near the double seal. The low tension current which is made and broken in the thermostat at B which operates the relay R (Fig. 1) is taken as a shunt from the 110-volt direct-lighting current by connecting the low-tension across adjacent taps on the 1,000-ohm resistance coil H. There are seven such taps along the coil and the potential difference between two adjacent ones is about 14 volts when the coil is in the 110-volt circuit. The current which actuates the sounder is made and broken by the relay. It passes from the relay through the 32-candle power lamp I, then through the electromagnets of the sounder, and back to the line, using the 110-volt direct current. The sounder is of the usual form, rated at 5-ohms, and heats but very slightly when the current passes through continuously. Except for the simple device shown for supporting the rubber tube, no other change in the sounder is necessary except that, if desired, the edges of the lever may be beveled so that the rubber tube is closed more easily. Small condensers, not shown, situated in the bases of the sounder and relay are used in lessening sparking when the currents are opened and closed in the thermostat and the relay respectively.

If cooling water is added at a rate very slightly more rapid than is necessary, the temperature is controlled with great exactness. Under these conditions, however, not enough cool water would be supplied should the room temperature rise considerably. On the other hand, if cold water is added too rapidly the bath becomes much undercooled at each addition. It has been found well so to regulate the supply that water is added to the bath about half the time. The temperature is then controlled within 0.1° C., irrespective of changes in room temperature.

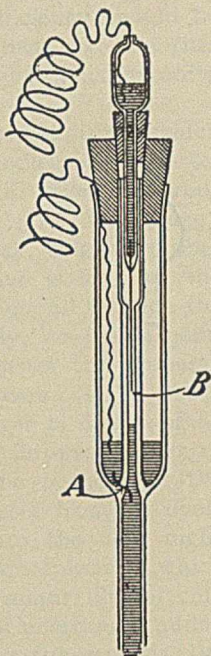


Fig. 2.

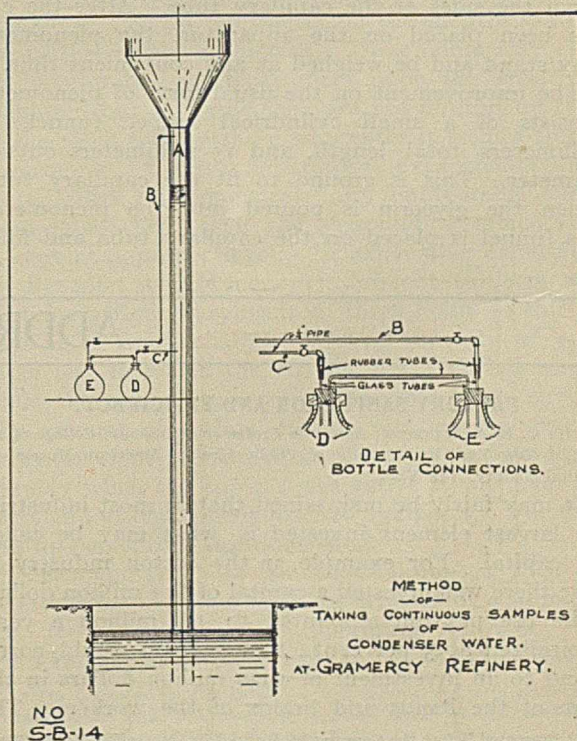
intervals of half an hour, as it leaves the condenser and as near to it as possible."

This method of intermittent sampling is the one usually employed. It will give a fairly satisfactory sample where entrainment in multiple effects is being studied. However, in the case of vacuum pans, in which the quantity and the viscosity of the boiling material are constantly changing, such a sample may fail to be representative.

The writer has devised an apparatus by means of which a sample may be taken continuously throughout any convenient period. It has been used successfully for two years. The accompanying print shows the arrangement.

"A" is the leg pipe of the condenser of the evaporator. "B" is a quarter-inch pipe entering the leg pipe near the top. "C" is a second quarter-inch pipe entering at any convenient point below the lowest level at which the water column in the leg pipe will stand when the evaporator is in use. These quarter-inch pipes project into the leg pipe about two inches. This prevents rust and dirt from the sides of the condenser from washing into the sample. "D" and "E" are heavy glass carboys. They are connected as shown in the small drawing. All connections must be air-tight.

When the valves on "B" and "C" are opened the sampling apparatus becomes a part of the vacuum system. The condenser water is forced through "C" into the carboy "D" by the pressure of the column of water in the leg pipe above "C." By manipulating the valves the water may be made to flow into "D" in a full stream or drop by drop as desired. "E" serves as a trap to catch any water from the upper pipe when the vacuum is broken.



AN APPARATUS FOR CONTINUOUS SAMPLING OF CONDENSER WATERS FROM EVAPORATORS.

By GEORGE P. MEADE.

Received May 16, 1911.

Mr. R. S. Norris, in his article on "The Determination of Sugar Lost by Entrainment from Evaporators" in THIS JOURNAL, October, 1910, gives the following method of sampling condenser waters. "Five liters of condenser water are collected, a liter at a time, at

The sample will stop running when the vacuum is broken but it will start again when the vacuum is sufficient to lift the column of water in the leg pipe above the level of "C."

Preparatory to taking a sample the rubber connection between "C" and "D" should be broken and the end of "C" immersed in a little clean water. The valve is then opened. The water will be drawn through the pipe and will clear it of rust and dirty water.

The carboys used must be carefully selected. There is danger of a serious accident if they are not sufficiently heavy to withstand the atmospheric pressure. As a precaution they should always be covered with bagging when in connection with the vacuum system.

CUBAN AMERICAN SUGAR CO.,
NEW YORK and CUBA.

AN IMPROVED PICNOMETER FOR GLYCERIN.

By L. W. BOSART, JR.
Received April 27, 1911.

The picnometer used is of cylindrical form, with thermometer ground in central neck, and with fused-in capillary tube at side.

The Geissler form with ground-in capillary may also be used if preferred.

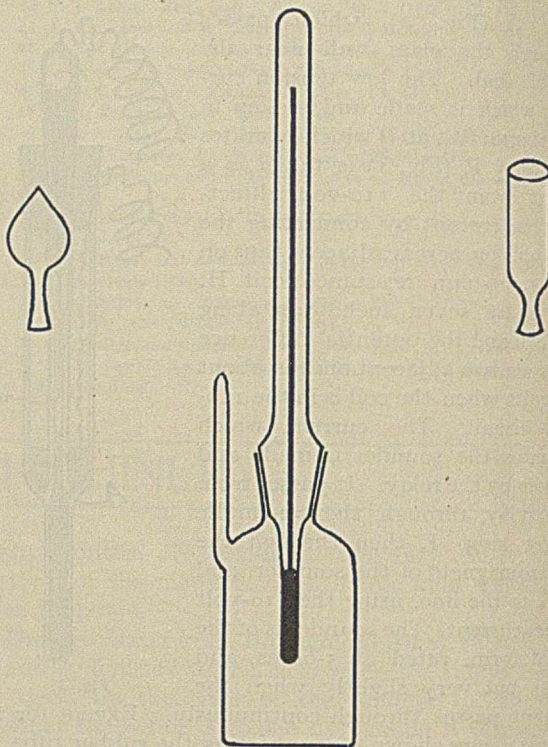
The cap which fits on the capillary tube as usually provided has no opening at the upper end and it is found expedient to attach a rubber tube to the lower opening of the cap, and hold the upper end in the small tip of a blast-lamp flame, while blowing through the rubber tube until a very small hole is blown through the glass.

By means of this hole, the air can escape when the glycerin expands and enters the cap and will not run down the sides of the capillary tube. After the cap has been placed on the apparatus, the picnometer may stand and be weighed at any convenient time.

The improvement on the usual form of picnometer consists of a small cylindrical shaped funnel, 38 millimeters total length, and 15 millimeters outside diameter. This is ground to fit the capillary tube. When the glycerin is poured into the picnometer, this funnel is placed on the capillary tube and filled

with glycerin and the determination can be made irrespective of whether the glycerin at the beginning of the operation is above or below the temperature at which the determination is to be made.

This is found to be much better than placing a rubber tube over the capillary glass tube, as is sometimes



done, as it is easier to see if the funnel is perfectly clean. It also allows for greater contraction of the glycerin and gives opportunity for better observations.

A cover made from the closed end of a test tube may be placed over the funnel to prevent any water being splashed in while the apparatus is in the bath.

Funnels of this description are made for us by Eimer & Amend, to fit the picnometers we had in use.

LABORATORY OF THE PROCTOR AND GAMBLE
MANUFACTURING CO.
NEW YORK CITY.

ADDRESSES.

FACTORY SANITATION AND EFFICIENCY.¹

By C. E.-A. WINSLOW, Associate Professor of Biology, College of the City of New York and Curator of Public Health, American Museum of Natural History, New York.

It may fairly be maintained that in most industries the largest element invested is what may be called life capital. For example, in the cotton industry in 1905 there was invested a capital of 613 million dollars while the pay-roll amounted to 96 million a year. Capitalized at 5 per cent., this pay-roll would correspond to an investment of 1920 million dollars in the form of the hands and brains of the workers. The

¹ Presented before the Congress of Technology, Massachusetts Institute of Technology, Boston, April 11, 1911.

calculation is perhaps a fanciful one; but it illustrates the fundamental fact that the human element in industry is of large practical importance.

Once the operative is trained and at work it is generally assumed that the results obtained will depend only on his intrinsic qualities of intelligence and skill. The effect of the environment upon him is commonly ignored, but its practical importance is very great. In industries where it has been shown that the machine which makes a given fabric requires certain conditions of temperature and moisture for its successful operation these conditions are maintained with exemplary care. In every factory, however,

there is another type of machine, the living machine, which is extraordinarily responsive to slight changes in the conditions which surround it. These conditions, in this relation, we habitually neglect.

I am not dealing now with the sociological and humanitarian aspects of the case. I am quite frankly and coldly, for the moment, treating the operative as a factor in production whose efficiency should be raised to the highest pitch, for his own sake, for that of his employer and for the welfare of the community at large.

The intimate relation between the conditions which surround the living machine and its efficiency is matter of common experience with us all. Contrast your feeling and your effectiveness on a close, hot, muggy day in August and on a cool, brisk, bright October morning. Many a factory operative is kept at the August level by an August atmosphere all through the winter months. He works listlessly, he half accomplishes his task, he breaks and wastes the property and the material entrusted to his care. If he works by the day the loss to the employer is direct; if he works by the piece the burden of interest on extra machinery has just as truly to be borne. At the close of the day the operative passes from an overcrowded, overheated workroom into the chill night air. His vitality lowered by the atmosphere in which he has lived, he falls a prey to minor illness, cold and grip and the disturbing effect of absences is added to inefficiency. Back of it all lurks tuberculosis, the great social and industrial disease which lays its heavy death tax upon the whole community after the industry has borne its more direct penalty of subnormal vitality and actual illness.

The remedy for all this is not simply ventilation in the ordinary sense in which we have come to understand the term. Mr. R. W. Gilbert, of the Massachusetts Institute of Technology, begins a suggestive paper on "The Economics of Factory Ventilation" in *The Engineering Magazine* for December last as follows: "Webster's definition of the word ventilation is 'to air' or 'to replace foul air by fresh.' In actual practice, however, ventilation should mean more than this. It should mean the conditioning of the air of any enclosed space to the best requirements of the occupants of that space." Conditioning of the air so that the human machine may work under the most favorable conditions—this is one of the chief elements of industrial efficiency as it is of individual health and happiness.

The chief factors in air conditioning for the living machine, the factors which in most cases far outweigh all others put together, are the temperature and humidity of the air. In many a plant money has been spent for an elaborate system of ventilation and if the air has been too hot or too dry or too moist the effect on comfort and efficiency has been worse than *nil*. It is a curious instance of the way in which we neglect the obvious practical things and attend to remote and theoretical ones, that for years more attention has been bestowed on the testing of air for carbon dioxide which was supposed to indicate some mysterious

danger than on the actual concrete effect of overheating. Heat, and particularly heat combined with excessive humidity, is the one condition in air that has been proved beyond a doubt to be universally a cause of discomfort, inefficiency and disease. Flugge and his pupils in Germany and Haldane in England¹ have shown that when the temperature rises to 80° with moderate humidity or much above 70° with high humidity, depression, headache, dizziness and the other symptoms associated with badly ventilated rooms begin to manifest themselves. At 78° with saturated air Haldane found that the temperature of the body itself began to rise. The wonderful heat-regulating mechanism which enables us to adjust ourselves to our environment had broken down and an actual state of fever had set in. Overheating and excess of moisture is the very worst condition existing in the atmosphere and the very commonest.

The importance of the chemical impurities in the air has dwindled rapidly with the investigation of recent years. The common index of vitiation due either to human beings or to lighting and heating appliances is carbon dioxide; but carbon dioxide in itself has no harmful effects in tenfold the concentration it ever reaches in ordinary factory air. Nor is there any reduction of oxygen which has any physiological significance. In the Black Hole of Calcutta and below the battened down hatches of the ship *London-derry* there was actual suffocation due to oxygen starvation; but this can never occur under normal conditions of habitation. It was long believed that the carbon dioxide was an index of some subtle and mysterious "crowd poison" or "morbific matter." All attempts to prove the existence of such poisons have incontinently failed. There are very perceptible odors in an ill-ventilated room, due to decomposing organic matter on the bodies, in the mouths, and on the clothes of the occupants. These odors may exert an unfavorable psychological effect upon the sensitively organized but as a rule they are not noticed by those in the room but by those who enter it from a fresher atmosphere. Careful laboratory experiments have quite failed to demonstrate any unfavorable effects from rebreathed air if the surrounding temperature is kept at a proper level. In exhaustive experiment by Benedict and Milner,² 17 different subjects were kept for periods varying from three hours to thirteen days in a small chamber with a capacity of 197.6 cubic feet in which the air was changed only slowly while the temperature was kept down from outside. The amount of carbon dioxide was usually over 35 parts (or eight to nine times the normal) and during the day when the subject was active it was over 100 parts and at one time it reached 231 parts. Yet there was no perceptible injurious effect.

The main point in air conditioning is then the maintenance of a low temperature and of a humidity not too excessive. For maximum efficiency the temperature should never pass 70° F. and the humidity

¹ The literature on this subject is well summarized with reference to original sources by T. R. Crowder in "A Study of the Ventilation of Sleeping Cars," *Archives of Internal Medicine*, 7, 85.

² Bull. 136. Office of Experiment Station, U. S. Dept. of Agriculture.

should not be above 70 per cent. of saturation. At the same time a too low humidity should also be avoided. We have little exact information upon this point but it is a matter of common knowledge with many persons that very dry air, especially at 70° or over, is excessively stimulating and produces nervousness and discomfort. It would probably be desirable to keep the relative humidity between 60 and 70 per cent.

Another point which may be emphasized in the light of current opinion is the importance of "perflation" or the flushing out of a room at intervals, with vigorous drafts of fresh cool air. Where there are no air currents the hot, moist vitiated air from the body clings round us like an aerial blanket, as Professor Sedwick calls it, and such of us is surrounded by a zone of concentrated discomfort. The delightful sensation of walking or riding against a wind is largely perhaps due to the dispersion of this foul envelope and it is important that a fresh blast of air should sometimes blow over the body to produce a similar effect. The same process will scatter the odors which have been noted as unpleasant and to some persons potentially injurious. The principal value of the carbon dioxide test to-day lies in the fact that under ordinary conditions high carbon dioxide indicates that there are no air currents changing the atmosphere about the bodies of the occupants.

There is one other problem of atmospheric pollution to which special reference should be made. The presence of noxious fumes and still more the presence of fine inorganic or organic dust in the air constitutes a grave menace to health in many processes and is an important contributory cause of tuberculosis. The normal body has its "fighting edge" and can protect itself against the tubercle bacillus, if given a fair chance, but the lung tissue which is lacerated by sharp particles of granite or steel quickly succumbs to the bacterial invader. In dusty trades like stone-cutting and cutlery working and emery-grinding, 75 per cent. of all deaths among the operatives are due to tuberculosis, against 25 per cent. for the normal adult population. This may be fairly interpreted as meaning that the actual death-rate from tuberculosis in these trades is from two to four times as high as in a corresponding average population; in other words, 3 or 4 or 5 out of a thousand of these workers are sacrificed every year to the conditions under which they labor. The elimination of the dust by special hoods and fans is imperative in such industries and must be supplemented in extreme cases by the compulsory use of respirators.

It is extraordinary how little is known to-day of the actual conditions of factory air, either by manufacturers or by sanitarians. So far as I am aware the New York Department of Labor is the only state department dealing with factory inspection which collects and publishes exact data in regard to the quality of the atmosphere in the workshops. If the conditions indicated in these reports by Mr. C. T. Graham Rogers are typical, and there is no reason to doubt that they are for the smaller industries at least,

there is urgent need for betterment. The table below shows that of 215 workrooms inspected 156 or 73 per cent. had a temperature of over 72°, and 63 or 29 per cent. exceeded 79°. In tabulating these analyses I have excluded all cases where the outdoor temperature was over 70°.

TEMPERATURE AND HUMIDITY IN NEW YORK FACTORIES.

Industry.	Number of work-rooms with temperature.			Relative humidity. Over 70 per cent.
	72° or less.	73°-79°.	80° or over.	
Printing.....	2	25	29	3
Clothing trades.....	9	23	7	6
Bakeries.....	1	20	15	7
Pearl button mfg.....	33	9	0	14
Cigar-making.....	8	4	5	7
Laundries.....	0	7	7	1
Miscellaneous.....	6	5	0	1
Total.....	59	93	63	39

In Massachusetts quantitative data of this kind are lacking, but the general results of inspection by the State Board of Health indicate similar conditions. In the report on the sanitary conditions of factories and workshop made by the Massachusetts State Board of Health in 1907, is the following comment upon the boot and shoe factory:

"In the majority of factories visited, the ventilation was found to be poor, and in many of them distinctly bad. Of the rooms not especially dusty, 102 were badly ventilated and 26 were overcrowded. In the rooms in which large amounts of dusts are evolved, the number of machines with means for efficient or fairly efficient removal of dust was found to be 1630; the number either inefficiently equipped or devoid of equipment was 2769.

"Of 84 of the many dusty rooms reported, 40 were also overcrowded, 35 were dark, 21 overheated, and 18 were overcrowded, dark and overheated. In more than one-third of the factories visited, the conditions of water-closets were not commendable; most of them were dark and dirty to very dirty."

There is plenty of evidence, though of a scattered and ill-digested sort, that the elimination of such conditions as these brings a direct return in increased efficiency of production. The classic case of the U. S. Pension Bureau is always quoted in this connection. The removal of the offices of the department from scattered and poorly ventilated buildings to new and well-ventilated quarters reduced the number of days of absence due to illness from 18,736, which figure it had been for several successive years, to 10,114.

In an investigation of my own of conditions in the operating room of the New England Telephone and Telegraph Co., at Cambridge, Mass., I found that before the installation of a ventilating system, 4.9 per cent. of the force (150-60 girls) were absent during the winter months of 1906 and 4.5 per cent. in 1907. The ventilating dust which was put in was a simple one and cost only about \$75.00 to instal but in the winter of 1908 following its introduction the absences were cut down to 1.9 per cent. of the force employed, without any other change in conditions or personell so far as I was able to discover.

¹ Report of the Commissioner of Labor for 1908, 1909 and 1910.

Mr. Kimball cites a number of similar cases in a paper on "Ventilation and Public Health" published in *The Annals of the American Academy of Political and Social Science* for March, 1911, the most striking of which are as follows:

"The Germania Insurance Company of New York in 1910 had eighty clerks in one office. Previous to the proper ventilation thereof, 10 per cent. were absent on account of illness all the while. Since then the absenteeism has been reduced to nothing.

"The vice-president of the Manhattan Trust Company of New York states that by proper ventilation he has so increased the efficiency of his clerical force that he has been able to reduce the number of employees 4 per cent.

"In a printing establishment in New York, a ventilation system was installed because of the insistence of the State Department of Labor that the law be complied with, the order having been resisted for two years. After the system had been in use a year the proprietor stated that had he known in advance of the results to be obtained no order would have been necessary to have brought about the installation. Whereas formerly the men had left work on busy days in an exhausted condition and sickness was common, now the men left work on all days in an entirely different condition, and sickness had been much reduced. The errors in typesetting and time required for making corrections were greatly reduced.

"Townsend, Grace & Company, of Baltimore, built a straw hat factory without ventilating apparatus. The first two winters after occupation the sick-rate was 27½ per cent. A ventilating system was then installed after which the winter sick-rate fell to 7 per cent. It was claimed that the ventilating system paid for itself in one year."

It is much to be desired that this problem should be studied by careful quantitative methods as a definite factor in the profit and loss account. The National Electric Lamp Association is approaching the question of sanitary conditions in this manner, comparing in detail the temperature and humidity of its work-rooms with the hours of work, the pay and the efficiency of its employees. Only by such systematic study can it be determined how much factory sanitation is really worth in any given case. The evidence is already strong enough, however, to warrant some investigation. In cases where preliminary study shows its value, why should not the sanitary inspection of a factory be made a part of its operation just as supervision of its mechanical features is a part of its organization to-day? It is not solely or chiefly the problems of ventilation as ordinarily understood that should be studied; and it must be remembered that there is never anything magical in a "ventilating system." "Systems" are as dangerous in sanitation as quackery in medicine. The problem must be approached from a broad biological viewpoint, and should include all the conditions which make for lowered vitality. Temperature and humidity come first and foremost and dust and fumes must be guarded against in certain processes. The cleanliness of the factory, the purity

of drinking water, the quality of lighting, the sanitary provisions and a dozen other points will suggest themselves to the skilled investigator when on the ground. He may find in many of these directions economic methods by which efficiency can be promoted.

The consulting factory sanitarian will be a new factor in industry but the progress of industrial economy and of sanitary science unite in pointing to the need for such an expert. If the manufacturers will fully utilize the resources of technology in this direction they can write a new chapter in the history of industrial efficiency.

REVIEW OF ELECTROCHEMICAL DEVELOPMENT.¹

By E. A. SPERRY.

Received April 24, 1911.

The fundamental factor in bringing about the era in which we live, the great factor which characterizes the present day and distinguishes it from ancient times, is the application of power. Authorities, the world over, agree to this. It is often stated as being the "introduction of machinery." But there would be little machinery without ready, cheap and practical sources of power.

In reviewing the early products in the various lines of activity, we are often struck with the wonderful ability exhibited in ancient times in the various branches; for instance, oratory and statesmanship were probably carried to as high a point as anything we can exhibit in modern times. We are also familiar with many examples of art and architecture produced in these early times, which equal, if not excel, examples of the present day, and even in matters relating to engineering; bridges and aqueducts were constructed, evincing wonderful knowledge in fundamentals. In many cases their dexterity excelled our own execution, for we must remember that an endless variety of implements, which to us are perfectly familiar and in every day use, were totally unknown to these early workers. In the realm of power, however, and its myriad applications, we have what probably constitutes the greatest single advance of modern times.

I do not think that any one will hesitate in agreeing also that this especial epoch, in the dawn of which we now live, is likely to be known as the age of electricity. It has fallen to my lot to be more or less intimately acquainted with the phenomenal and wonderful advances in this field, advance taken by *leaps* and *bounds*; in single decades advances have been made equal to whole centuries in many other lines of activity.

In the spring of 1884 I became the only Western delegate to come to this city from Chicago, to help in organizing the American Institute of Electrical Engineers. A small group of us gathered in the modest rented quarters of the then young society of Mechanical Engineers, on 23rd Street, and I became the fifth to sign the charter and placed my money on the table in the original act of organization of that society. A

¹ Address before the annual meeting of the American Electrochemical Society, New York, April 7, 1911.

small group of earnest men builded wiser than they knew in thus organizing a society which has since become a body of international importance, and one doing much in the direct advancement of science and art in this important field, with its myriad branches and avenues of activity. Its members now number upwards of seven thousand.

It must be remembered that at this time the only practical and commercial application of electricity was in lighting. In the Spring of the next year it so happened that I was Chairman of the Committee of Call of the first Convention of the National Electric Light Association, which we organized in the City of Chicago in 1885, and which is now a flourishing organization, having some eight thousand members doing a vast work in many fields of practical application of electricity, especially leading in the work of conversion of all natural sources of power throughout this country.

The topics and subjects brought up for discussion at this first Convention would have amused, if not amazed, this present audience. Earnest questions as to the possibility of being able to use electricity as a motive power, and recounting disastrous results in trying to use the few small electric motors of the time, all give a vivid idea of the struggles and discouragements of those pioneer days.

The art and industry which we foster represents the most direct and most recent development of this great advance movement in the application of power, in that we bring power or energy in its most controllable, as well as its most active form, name *electricity* to bear upon chemical actions and reactions, resulting in many fields, in a much more direct and economical solution of the problems involved; in numerous instances, in products otherwise unattainable and working economies which at once place valuable elements and compounds within reach of all, thus rendering great service to mankind.

Electrochemistry as such may be said to be largely American in its origin, and emphatically American in its practical development. I speak advisedly on this point. Our great water power resource and development are not alone responsible for this, the enterprise and enthusiasm of our technical and commercial men have played no small part in this great work. Such names as those of Castner, Hall, Wilson, Atcheson, Herreshoff, Townsend, Dowe, and a host of others testify to this. As to this art being American in its large practical development, one has only to recount the numerous chemical processes we have imported bodily from Europe, and almost without change adopted. Outside of this long list it should be remembered that we are still currently importing a large amount of chemical products. The contrast with this quite strikingly emphasizes the point we make that in the field of electrochemistry we have been enabled to very largely supply the entire demand for electrochemical products and cut down very materially, if not entirely, importation.

The value of the electrochemical, as compared with

the purely chemical method, is illustrated by the "Solvay" process which was imported from Belgium and which employs as its principal raw material, sodium chlorid, or common salt; but in the operation of this process only one of the elements of this valuable compound, namely the sodium, is recovered. Our State was recently called upon to condemn and to relinquish a lake of quite considerable size, for receiving the deposit containing the other element, namely chlorin, which is a waste product rejected in this process. In a number of electrolytic plants in this country where the same raw material is employed, practically 100 per cent. of both of these constituent elements are recovered and rendered available and useful, certainly marking an advanced movement in the point of conservation of our mineral resources. This illustrates one only of the advantages following the direct application of electricity in processes that are known as "electrolytic." Our good Mr. Herreshoff here present tells me that practically 90 per cent. of all the copper that is used in the world is refined electrolytically. Seventy or 80 per cent. of the original copper contains arsenic, minute quantities of which are known to degrade copper and render it practically useless as an electrical conductor. The electric arts employ about 70 per cent. of all the copper produced; thus the circuit may be said to be closed in two ways—the electrolytic ministering to the electrical.

There is quite a dramatic aspect connected with this electrolytic copper refining not popularly understood. Think of nine hundred thousand tons of this beautiful, glistening, red massive metal existing as a perfectly clear, watery solution in one stage of its life history, during its transit from anode to cathode after it has been dissolved by the direct action of electrical energy in the electrolyte!

Started in Germany, this process was taken up actively in England, but now it may be said that America is its home; certainly, by far, its greatest activity is to be found here, and we have here present probably the greatest worker in this art; certainly the one who has brought to its highest perfection electrolytic copper refining.

Again, electrolysis has given the world aluminum. Only a few years ago this metal was \$6.00 a pound. Then it gradually came down to \$1.00. The engineering world then gave its use the first passing thought. Hall in this country and Heroult abroad, working on and on, through many discouragements, succeeded finally by its electrolytic production; by the direct application that this method affords, in supplying the energy for which this element has an enormous appetite, and so reducing its cost as to place it within reach of all. In consequence, its industrial applications have broadened, until 50,000 tons, valued at \$20,000,000, are annually consumed. This metal also, like the copper, is in the form of a perfectly clear solution in one stage of its life history, with this difference, however: that in the case of the copper, the solution stage constitutes what may be termed its "graduation certificate," whereas with

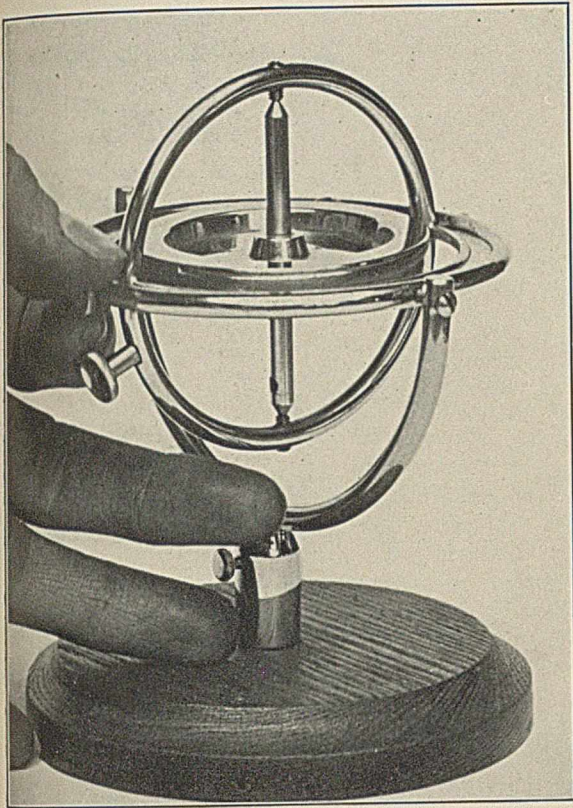


Fig. 1.

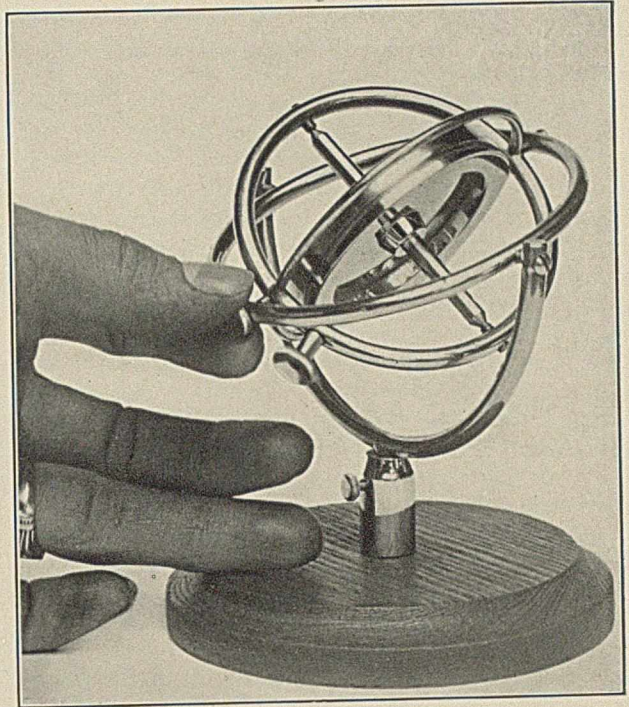


Fig. 2.

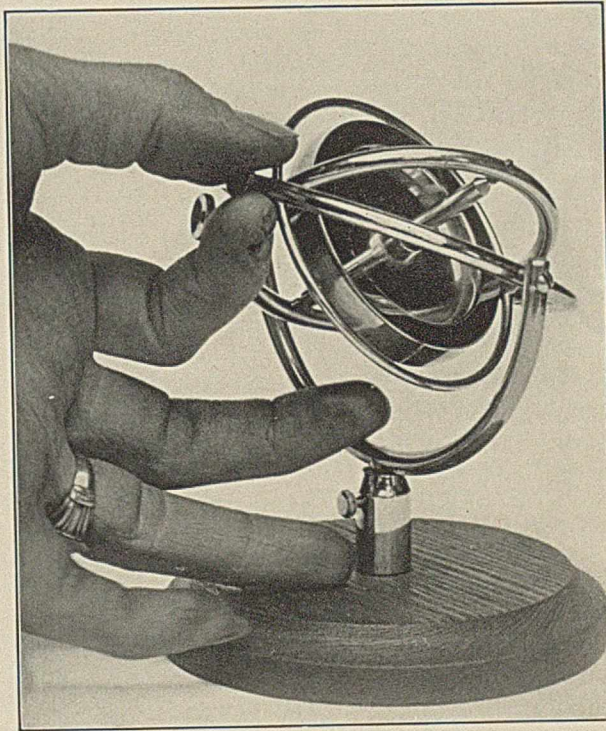


Fig. 3.

aluminum, it is even more far-reaching and actually constitutes its "birth certificate."

I might go on numerating interesting examples of these direct applications of electricity for producing chemical reaction, both in electrochemical and thermal applications which constitute the principal activities and interests of our members. For instance, a most valuable product, calcium carbide, would not exist were it not for the electric furnace, this process having been discovered and brought out in this country by Mr. Wilson.

One fact which arrested my attention, however, and for which I crave your indulgence for a moment more, is a fact brought out recently by the noted authority in the field of original research, the next speaker, Dr. Whitney, of Schenectady, when he stated that it was a fortunate circumstance when bodies were energized or otherwise induced to react, they did not directly tend, in the majority of cases, to reproduce the energy, or energy of the same form; for instance, reactions do not tend directly to produce heat, but, on the contrary, when energy, such as heat or electricity, is applied and a reaction takes place, a new compound is produced, that is, the operation "side-steps," so to speak, bringing about a new, and, broadly speaking, an unexpected result. This phenomena of indirection, as it may be called, seems to me to be a general law, a sort of a by-pass which nature takes in producing variety.

It may be stated that this is the manner in which variety occurs. So universal is this method that, as a matter of fact, it is difficult to obtain a reaction which *does* give back the energy in the same form as applied, *e. g.*, the delicate processes necessary in constituting what is known as the storage battery, whereby electricity may be again returned after first having been introduced.

The universal law seems to be one of translation instead of oscillation. In fact, upon introduction, stresses will give you almost anything except a return of the particular stress, qualitatively. This phenomena having such a very striking and complete homologue in a totally different branch of science and one to which I have devoted considerable attention, I may be pardoned if I bring it to your attention by the use of a model which serves to illustrate in a most vivid way just what I mean. I hold before you a gyroscope having Cardan or universal mountings. The outer ring being pivoted, I now swing it back and forth, and we see the inner ring which is mounted therein and its wheel simply partake of the same motion, and that nothing whatever peculiar occurs, that is, all of the parts move together, just as they should, back and forth, upon the pivots of the outer ring. But suppose I now spin up the wheel within its inner ring and repeat the same operation, that is, attempt to swing the outer ring to and fro upon its pivots as before. Our attention is at once arrested by the very peculiar, vigorous and unexpected motion which the inner ring now makes. It is

evident that this motion is not only automatic, being self-developed, but it seems to bear no relation whatever in this direction to that of the impressed forces, and upon close examination we find that it exists to the normal, or actually at right angles to the line of the original energization. As a matter of fact, it "side-steps," and this it does invariably. With each application of stress in a given line or plane, the inner ring moves to and fro in a plane at right angles, "side-stepping," so to speak, under the impressed stress, and in a line or direction just as far removed from that of the impressed forces as it is possible for it to do, namely 90° measured either uniplaner or as a spherical function. Here we have this phenomenon in a form which we can handle, study, weigh and measure. The homologue, I believe, has a very far-reaching significance and one which I cannot but believe derives its fundamental activity in this devious path from the same underlying principle, namely *rotation*. It need not be rotation about its own axis, as in the case of the inner wheel before us, but it may be rotation about a remote center of which the observer has no knowledge, nor the existence of which he even suspects, yet all that is required is the presence of rotation or angular velocity, and when this is present in either ion, atom, molecule or mass, there invariably exists a definite and powerful tendency; a definite ponderable moment of effort in this new direction to one side practically at right angles to that of the stress or forces impressed. These phenomena are not only qualitatively analogous, but I believe them to be quantitative and determinable.

Nor should we look upon such a solution of this action which seems almost universal, as less significant. When we remember that motion itself is universal, all nature seems to be either in a state of motion or consisting of motion in its deeper significance.

As the underlying principles of these motions are better understood, why should we not be able to assign definite values, to pre-cast definite directions in which the movements or reactions should proceed, and with the same degree of precision that we are now enabled to apply in that branch of the useful arts in which this self-same phenomenon is fundamental, is just now in rapid state of development and is destined to become an extremely important and useful force in the service of mankind?

I hope that this seeming digression may be pardoned. By the use of the model I have endeavored to make clear to you the true nature of this phenomenon; the strange, physical reaction which we know as gyroscopic precession. Knowledge of this action was made use of by our great contemporary, Sir J. J. Thompson, in a number of notable observations made not long since, and I am hoping that it may so impress itself upon your minds as to be equally useful to you. It should not be understood that the observations and statements I have made are put forward as being in any way final, but are intended to be more in the line of suggestion.

THE CHEMIST IN THE SERVICE OF THE RAILROAD.¹

By H. E. SMITH.

Received April 20, 1911.

Among the industries of the country, the railroads are probably the largest, whether they be judged from the standpoint of investment required, territory covered, or men employed. Considered as manufacturing establishments, the railroads use as raw materials, iron and steel of all kinds, brass, bronze and babbitt, wood and timber of all kinds, stone, brick, cement, oils and paints, and a great number of materials of lesser importance. The manufacturing process covers various departments of field engineering, power production, shop work and metallurgy. The finished product is the transportation of passengers and freight.

As in numerous other manufacturing industries, the equipment required is constantly becoming heavier, more elaborate and expensive. The methods of operation are constantly becoming more complicated, more specialized and more costly, yet the piece price of the product, transportation, is constantly diminishing.

This condition evidently necessitates increasingly scientific management and operation. The need of the civil, the mechanical and the electrical engineer is obvious. With the increasing development has come the need of the chemist and, beginning nearly thirty years ago, the Massachusetts Institute of Technology has at various times furnished chemists for this service.

As has already been partially indicated, the field for the chemist in railroad service is very wide. Early in the construction of a first-class road the chemist is in demand for the testing of cement, to ensure sound and durable concrete bridges and other structures; in the selection of ballast stone of such composition and physical properties that it will withstand the weather and the impact and wear of service. Timber for cross ties now commands such a price that economy necessitates preservative treatment by carefully tested and regulated materials and processes. Rails must be of such composition that they will resist wear in the greatest possible degree, yet be free from brittleness.

The problem of boiler water supply, especially that for locomotives, is of very great importance. An average modern locomotive is a complete power plant of 2000 horse power, mounted on wheels, and contained within a space only a fraction of that required by a stationary power plant of the same capacity. About one hundred gallons of water are evaporated per mile traveled. In many parts of the country the only water available is of such quality that economy in operation requires its chemical purification. This brings to the chemist the problem of carrying out chemical reactions on a large scale, and in extremely dilute solutions, yet with very close adjustment and at low cost.

Iron castings are used in such quantities that railroad companies frequently make their own. The

pig iron and the coke must be tested to ensure proper quality. The mixtures must be adjusted to secure the necessary product. Car wheels must be tough and strong yet very hard on the circumference, to resist wear. Machinery castings must be strong yet machine easily. Packing rings must be very resilient. Yet in all mixtures economy must be practiced by using up scrap.

The proper selection of steel for efficient and economical service is a constant problem. Special alloy steels, either with or without special heat treatment or other manipulation, are used in increasing quantities. It is necessary to make very frequent and systematic chemical and physical tests to ensure uniform and satisfactory quality.

Large quantities of brass or bronze, mostly in the form of bearing metal, also babbitt for the same purpose, are required. The prices of the constituent metals vary from five to thirty-five cents per pound, which constitutes a strong temptation to substitute the cheaper for the more expensive, so far as possible. The chemist must be called upon to detect such substitution and to determine whether the constituents have been properly proportioned. Scrap must be utilized and the chemist is needed to test the remelted metal and adjust its composition to standard figures.

Paints are used in large quantities on cars, buildings, bridges, etc. The pigments are frequently adulterated with inferior, inert or injurious minerals, the linseed oil with petroleum and inferior vegetable oils, and the turpentine with benzine. The proportions of the specified ingredients must also be checked. Lubricating and burning oils constitute another important class of material for study, to secure the proper selection of grades and maintenance of satisfactory standards.

The list of articles which come up for occasional attention includes soaps, greases, roofing materials, fireproofing materials, various chemicals, minerals and ores, rubber, battery materials, dyestuffs, inks, grinding and polishing materials, disinfectants, rope, cotton and woolen waste, fuel, etc.

Not only must all these materials be examined after purchase, but many of them must be bought on definite specifications in order to secure the desired quality under competitive bids. The writing of the specifications falls chiefly upon the chemist. To this end he must study carefully the needs of the service, the quality of material best adapted to meet those needs, as well as the quality available on the market, and finally the methods of test best adapted to determine the quality. This exhaustive study may also be the means of ultimately developing or improving various industries so that it is beneficial not only to the consumer but to the producer.

It is natural that the chemist should also be required to study various methods and processes of operation in different parts of the railway service, with a view to the economy of material or labor or to increasing the efficiency of the service.

In all the work above described, the investigator must be more than a chemist. He must be some-

¹ Read before the Congress of Technology, Massachusetts Institute of Technology, Boston, April 11, 1911.

thing of a geologist, a physicist, a metallurgist, an electrician or a sanitarian, as the case requires, and withal must have the ability to predict the effect from the cause, or to trace back from the effect to the cause.

It is for these reasons that the broad and comprehensive training offered by the Institute of Technology is especially adapted to fit men to take up scientific work for the modern railway.

SCIENTIFIC SOCIETIES

SOCIETY OF CHEMICAL INDUSTRY.

Annual general meeting to be held in Sheffield, England, July 12-13-14, 1911.

PROGRAM.

WEDNESDAY, JULY 12TH.

Morning.

- 10 A.M. Council Meeting at the Cutlers' Hall.
10.30 A.M. Annual General Meeting and Address by the President.
1 P.M. Luncheon at the Grand Hotel, Leopold Street, by invitation of the Yorkshire Section.

Afternoon.

Visits to the following works:

- Peter Dixon & Son, Paper Mills, Oughtibridge.
- The Sheffield Simplex Motor Works, Tinsley.
- James Dixon & Son, Cutlery and Silver Works, Cornish Place.
- Tennant Brothers, Ltd., Brewery.
- W. S. Laycock's Railway Carriage, Steamship, and Tramcar Fittings Works, Millhouses.
- Thomas Firth & Sons, Norfolk Steel Works, Savile Street, East.

Evening.

Annual Dinner at the Grand Hotel, Leopold Street, at 7.15 for 7.30. Tickets, excluding wine, 7 s. 6 d.

THURSDAY, JULY 13TH.

Excursion.

Newton Chambers & Co., Thorncliffe, and the Wharnccliffe Silkstone Colliery, Tankersley.

Including:

- Koppers Retort Ovens and By-Product Plant.
- Manufacture of Izal Disinfectant.
- Demonstration of Life-saving Appliances in an Irrespirable Atmosphere at the Rescue Station.
- Simon-Carves By-Product Coke Ovens and Utilization of Surplus Gas for Power Purposes.

Messrs. Newton Chambers & Co. will provide lunch. Return tickets 1/6 each.

EXCURSIONS.

Morning.

- The Grimesthorpe Works of the Sheffield United Gas Light Co.
- John Brown & Co., Atlas Steel and Iron Works.
- William Cooke & Co., Ltd., Tinsley Steel, Iron, and Wire Rope Works.
- William Hutton & Sons, Cutlery and Plate Works, West Street.

(e) Mappin & Webb's Cutlery and Silver Works, Norfolk Street.

(f) The Metallurgical Department of the University of Sheffield, St. George's Square.

Afternoon.

- Cammell Laird & Co's. Grimesthorpe Steel and Iron Works.
- Vicker's River Don Steel Works.
- Park Gate Iron and Steel Works, Rotherham.
- Steel, Peech, & Tozer's Phoenix Special Steel Works, The Ickles.
- Joseph Rogers & Sons Cutlery and Silver Plate Works, Norfolk Street.
- Walker & Hall's Cutlery and Silver Plate Works, Howard Street.

Evening.

Reception by the Lord Mayor and Lady Mayoress at the Town Hall at 8.30 P.M.

FRIDAY, JULY 14TH.

Excursion.

Drive over the Derbyshire Moors, visit to Chatsworth House and Grounds, and Haddon Hall, returning by Bakewell. Inclusive tickets 12/6 each.

Evening.

9 P.M. Smoking Concert at the Grand Hotel.

A detailed program with request form will be issued with the June 15th number of the Journal.

Ladies are invited to all the fixtures.

All communications should be addressed to the Secretaries, 67 Surrey Street, Sheffield.

THE PITTSBURG MEETING OF THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS.

The meeting was an unusually important and successful one, both with respect to the attendance—some 600 members and guests being registered—and the value and interest of the papers considered at the technical sessions.

Three afternoons were devoted to excursions to various industrial plants in the vicinity of Pittsburg.

The meeting was opened on Tuesday evening with an informal reception of the visitors in the Schenley parlors, at which one notable event was the presentation to the President of the Society, Col. E. D. Meier, of an engrossed testimonial expressing the high regard of the members of the Society for Col. Meier's professional attainments and personal character. The presentation was made appropriate by the fact that the day was Col. Meier's 70th birthday. Those joining in presenting this testimonial to Col. Meier have arranged to have his portrait painted.

The regular work of the convention began on Wednesday morning with the semi-annual business meeting. The only matter of particular interest taken up at this meeting was the report of a committee which presented a schedule of standard dimensions for flange pipe fittings of all sizes, from 1 $\frac{1}{4}$ inches to 24 inches, both for standard weight pipe and extra heavy pipe. These standards were prepared jointly by a committee of the National Association of Master Steam and Hot Water Fitters and a committee of the American Society of Mechanical Engineers. The standards will be printed and made available for those interested.

The Society is inaugurating a new departure in an endeavor to adequately cover a number of specialized fields of work, in which the mechanical engineer's work has become of great importance. Through the Society's Meetings Committee, special committees are being organized, each one of them having responsibility for a certain particular branch of mechanical engineering. The engineering of cement manufacture is one of these branches, and the morning was spent in consideration of a number of papers relating to this field.

NATIONAL ELECTRIC LIGHT ASSOCIATION.

The thirty-fourth convention of the National Electric Light Association, which was held at the Engineering Societies' Building, New York, from May 29th to June 2nd, inclusive, broke all records for attendance, over 5,000 members and guests being registered. The meeting was made up of 16 sessions, divided between general, commercial, technical, accounting and power transmission, three parallel sessions being the rule. Numerically the commercial section sessions were the most attractive to the delegates, and although the smallest of the halls was allotted to the accounting sessions, this was not true of the attendance. In addition to the regular chapters a meeting of the Public Policy Committee was held at the New Theater, and there Mr. Samuel Insull read the set report of the committee, which concerned the various forms of welfare-co-partnership and insurance work among employees. This was followed by an address by Hon. Charles Nagle, Secretary of Commerce and Labor, who lauded the proposals of the committee, claiming that the adoption of them would go a long way toward warding off unwise legislation.

PHARMACOPOEIA TRUSTEES.

The first annual meeting of the Board of Trustees of the United States Pharmacopoeial Convention for the term of 1910-'11 was held at Philadelphia on May 5th and 6th, with the full board in attendance. Prof. James H. Beal, of Pittsburg, was elected chairman, and Dr. Henry M. Whelply, of St. Louis, secretary. The accounts of the treasurer showed that he had received a balance of \$8,394 from his predecessor, the treasurer from 1900-1910. The sales of the English edition for the fiscal year ending April 30, 1911, amounted to \$6,188 and of the Spanish edition to \$1,169. Two hundred and ninety dollars were received as royalty from the use of the text and \$172 as interest, making the total receipts \$16,213. The total expenditures, including the expenses for the convention of 1910, amounted to \$7,874, leaving a cash balance on hand of \$8,339.

INTERNATIONAL AGRICULTURAL CONGRESS.

The International Agricultural Congress has decided that the tenth Congress shall take place in Belgium in 1913. A preliminary meeting will be held in Paris next year.

The Rumford Prize of the American Academy of Arts and Sciences was awarded to Prof. J. M. Crafts for his studies in high temperature thermometry at the recent annual meeting of the Academy.

Prof. Jacques Loeb, of the Rockefeller Institute, has been elected a correspondent of the Academy of Natural Sciences of Philadelphia.

The fourteenth annual meeting of the American Society for Testing Materials was held in Atlantic City, June 27th to July 1st.

The annual meeting of the National Commercial Gas Association will be held on October 23, 1911, in Denver, Colo.

The International Acetylene Association will hold its annual meeting in August, 1911.

EDUCATIONAL

SPECIAL COURSE IN HIGHWAY ENGINEERING.

The Trustees of Columbia University announced at their June meeting the establishment of a new course of instruction in Highway Engineering and have called Arthur H. Blanchard, of Brown University, as Professor of Highway Engineering.

The establishment of this course is due to the widespread interest in the cause of good roads and the

need of a closer scientific study of the various problems involved in road materials and construction. It is believed that systematic instruction in the fundamental principles of highway engineering will lead to standardization and improvement.

The success of this course in Highway Engineering has been insured by the gift of \$10,000 annually for five years from Mr. Charles H. Davis, C.E., '87.

EUROPEAN SCHOOL STATISTICS.

Consul General T. St. John Gaffney reports that there are 465,451 schools with 45,500,000 pupils in Europe, presided over by 1,119,413 teachers. According to the average, there is 1 teacher to every 45 scholars. Twelve years ago there was only 1 teacher for every 60 scholars. The number of teachers in Russia is about 195,000, while those in Germany number 168,000. In Russia there is 1 teacher to every 644 inhabitants, and in Germany there is 1 teacher to 361. In England there are 177,500 teachers occupied, which allows 1 teacher to every 234 inhabitants. In Germany there are 3 illiterates to each 1,000 of population, while in England the reare 10. The most illiterates are to be found in Russia, where there are 617 to every 1,000 inhabitants. In Germany 68 per cent. of the attendance at the schools is composed of children between the ages of 5 and 15; in Russia the average is only 27 per cent.

Mr. T. C. DuPont has given \$500,000 to the Massachusetts Institute of Technology toward its proposed new site. Announcement is also made of a trust fund of between five hundred and six hundred thousand dollars, created by Francis B. Greene some five years ago, for the assistance of students, and \$500,000 from the bequest of Mrs. Emma Rogers, widow of William B. Rogers, the first president of the institute. These large gifts, in addition to the \$100,000 for ten years appropriated by the state, will make it possible for the institute to purchase a new site and erect the necessary buildings.

Governor Foss has signed the bill by which the Massachusetts Institute of Technology will receive \$100,000 annually from the state for ten years. By the terms of the measure the Institute will maintain 80 free scholarships to be apportioned among the 40 senatorial districts of the state.

The H. F. Kieth Company, of Boston, have given \$5,000 to the Massachusetts Institute of Technology, for a research on the decomposition and general

wholesomeness of eggs and for an investigation of the bacterial and chemical content of the product under varying conditions.

Dr. Bertram B. Boltwood, professor of radio-chemistry at Yale University, was elected to membership in the American Philosophical Society at its recent meeting, as was also Dr. A. A. Noyes, professor of physical chemistry at Massachusetts Institute of Technology.

Dr. Theodore William Richards, professor of chemistry at Harvard, who is going to England at the invitation of the Chemical Society to deliver the Faraday lecture, will be given the honorary degree of D Sc. by the University of Manchester on July 8th.

During his presence in New York City Dr. Svante Arrhenius lectured at the College of the City of New York on the afternoon of May 17th, at the Chemists' Club on the evening of May 17th and at Columbia University on May 18th.

Prof. Charles H. Fulton has resigned the presidency of the South Dakota School of Mines, Rapid City, S. D., and is going to the Case School of Applied Science, Cleveland, Ohio, as professor of metallurgy and head of its mining department.

Lieut. Col. W. Robinson, of the U. S. Army, has been nominated by President Taft to be professor of chemistry at West Point commencing October, 1911, to succeed Col. S. E. Tillman who will retire then.

Dr. W. F. Watson, professor of chemistry and biology in Furman University, Greenville, S. C., has resigned the chair which he has occupied since 1890.

Dr. C. F. Mabery, professor of chemistry in the Case School of Applied Science, has resigned the chair which he has held since 1883.

OBITUARIES

NATHANIEL WRIGHT LORD.¹

1854—May 23, 1911.

Nathaniel Wright Lord, born at Cincinnati, Ohio, December 26, 1854, sprang from a notable ancestry. His father was Henry Clark Lord, a man prominent in the business and political life of his time, and son of Nathan Lord, for many years President of Dartmouth College; his mother Eliza Burnet Wright, a woman of rare vigor and ability.

Professor Lord's education was begun in the public schools of his native city, and their training, developed by a year of searching review under an ex-

acting foreign tutor of rare gifts, was enlivened by frequent boyish forays into fields of natural history. Hence, the rigorous course in mining engineering taken 1872-76 at Columbia College School of Mines caused him no difficulty. Next came a year of hardship in Central American mining, which nearly cost him his life. Upon his return and recovery the young engineer was appointed, November 6, 1878, State Analyst at Ohio State University. On June 18, 1879, the Department of Mining and Metallurgy was entrusted to him, and remained under his control until the end of his life.

Professor Lord's professional career was largely developed in the service of this institution. His

¹ Memorial adopted by the Faculty of Ohio State University in special session May 24, 1911.

earliest engineering experience as the chemist and technical director of a Gold Mining Company in Nicaragua, though it had been of great service in developing his power and self-confidence in the application of science to engineering, yet had given him little reputation. In the new position his ability and energy were soon recognized. He became, in 1883, chemist of the Geological Survey of Ohio, contributing in addition to his chemical reports valuable chapters on the iron industry and on the differentiation of the coal seams of the state by novel methods. His grasp of these subjects was so masterly that he became a national authority on fuels and fuel-testing, and for the past eight years has been chief chemist or consulting expert of the Technologic Branch of the United States Geological Survey, now the Bureau of Mines.

Upon the College of Engineering, Professor Lord has left an enduring mark. As its first Dean, beginning in 1896, he carried it through its formative period, and left it with policies and ideals well crystallized. His sane and practical mind rejected instantly everything that savored of show or pretense. As in his engineering, so every educational plan must rest upon a solid foundation. His constant struggle was to ground his students thoroughly—well assured that upon such a foundation they would erect a secure superstructure. His teaching was a constant appeal to the reason, and to the constructive imagination. To see him with a class attack a problem new to both was a rare experience.

Combined with his power and inspiration as a teacher, was his pre-eminent ability as an investigator. The training of the chemical laboratory, where everything must be accounted for, gave to his naturally incisive thinking processes a precision and analytical power most unusual. No man could with more unerring certainty strip a complicated problem of its

disguises and lay bare its fundamental principles. No field of science upon which he touched failed to profit in some enduring way from his ever active mind.

No man could associate with him in any capacity without admiring him; his large mind and generous spirit had no room for anything little or sordid. Creditable, useful, even brilliant, as many of his contributions to science and engineering have been, his influence on his students and on his colleagues is the signal proof of his greatness.

To the very last he was a man of diversified interests and continually entered upon new pursuits with characteristic enthusiasm.

Professor Lord was a man of marked intellectual vigor. His mind was no less judicial than analytical. He thought clearly and spoke with logical precision. In action he was prompt, decided and fearless. His moral convictions rested upon reason rather than upon authority or tradition.

With the reserve of a gentleman who permitted no undue familiarity, he yet remained essentially democratic, and no one felt humbled in his presence. Honesty was fearless before him. To those who won his confidence, he was a loyal friend and a wise counselor.

In the death of Professor Lord this Faculty mourns the loss, not merely of their colleague of longest unbroken service, but of the brilliant man of science, the incisive and powerful teacher, the keen yet broad-minded counsellor, the vigilant and strong supporter of the university, the loyal citizen, delightful companion and generous friend, the man of rare quality, originality and broad interest, whose place in the hearts of those who knew him intimately, can never be filled.

S. C. DERBY,

WILLIAM R. LAZENBY,

EDWARD ORTON, JR.

NOTES AND CORRESPONDENCE.

CONDENSATION PRODUCTS OF PHENOLS AND FORMALDEHYDE.

To the Editor of the Journal of Industrial and Engineering Chemistry.

SIR:

In the June number, 1911, of THIS JOURNAL, reference is made to phenol-formaldehyde condensation products invented by Mr. Aylsworth.

I am unable to find in the chemical literature any publication of Mr. Aylsworth relating to this subject, except a Belgian patent application dated February 11, 1911, No. 232,899, claiming International Convention Priority of one year, in accordance with a corresponding United States patent which has been applied for.

Belgium is one of the countries where patents are allowed without any preliminary examination whatever as to novelty, and where, furthermore, no restriction is put on the claims, nor the text of the patent,

the granting of the latter being a mere formality which places the claims of the applicant on record.

For persons who are not acquainted with the technical and chemical side of the subject, the long text of Mr. Aylsworth's Belgian patent is undoubtedly very complicated and liable to mislead. But when we come to the question of novelty, we find that the principal claim has for object the preparation of a hard, infusible condensation product by adding formaldehyde or its equivalent to a fusible phenol resin.

It so happens that this reaction was clearly disclosed in THIS JOURNAL about one year before the Aylsworth patent was filed: (See *Journal of Industrial and Engineering Chemistry*, Vol. 1, No. 8, August, 1909, L. H. Baekeland, "On Soluble, Fusible Resinous Condensation Products of Phenols and Formaldehyde," read May 14, 1909), from which I quote:

"In whatever way novolak be prepared, its properties are very distinct from those of bakelite and it cannot be transformed into the latter by simply heating. But I have found that by heating novolak in sealed tubes at 180° C., under pressure with an excess of formaldehyde solution or any of the polymers of formaldehyde or other compounds which can generate formaldehyde, an infusible, insoluble mass is obtained that does no longer soften under the action of heat, as is the case for saliretin products, but which has all the characteristics of bakelite C."

The term novolak was the generic proposed name to designate all fusible soluble condensation products of phenols and formaldehyde of the type designated by Aylsworth as "phenol resin" or "resine phenique."

Furthermore, in patents granted to Baekeland in France (first addition to Patent 386,627, No. 11,628, filed January 22, 1909) and in Belgium (No. 213,576, published February 15, 1909) the invention is disclosed as follows:

"L'inventeur a trouve egalement que, au lieu de partir des phenols et de la formaldehyde, on peut commencer indirectement avec l'emploi d'un phenol-alcool ou ses equivalents, chauffant sept molecules de ce dernier avec au moins une molecule de CH_2O , ou une quantite equivalente de n'importe quelle substance contenant de la formaldehyde, ou capable de liberer cette derniere."

The "phenol resin" of the Aylsworth specification answers all the descriptions and all the properties published by Blumer. (See Eng. patent June 5, 1902, No. 12,880) and DeLaire (see French patent June 8, 1906, No. 361,539) and the description set forth in Baekeland's prior publication in THIS JOURNAL.¹

It is true that in the Aylsworth Belgian patent it is claimed that the fusible phenol resin has a molecular weight smaller than what I assigned to these products. On the other hand, it is stated that the molecular weight proposed by Mr. Aylsworth is based on "quantitative synthesis," whatever that may mean.

It should be pointed out that we have to deal here with substances which are amorphous, non-crystalline, non-volatile, and can not be purified by the usual ways. Furthermore, in any of these reactions, several substances are liable to be produced at the same time. These substances can form solid solutions one with another, or with any excess of the reacting materials employed.

Under the conditions, so-called "quantitative synthesis" would hardly be accepted in any scientific controversy, and specially not for determining the molecular weight.

The same can be said of any attempt to apply the other usual physical methods for the determination of molecular weights to similar substances unless the latter have been submitted to thoroughly careful purification. To omit this precaution would bring about such absurd results that it would only depend upon the operator to get almost any desired molecular weight by increasing for instance the amount of free phenol.

But the fact is undeniable that the physical and general chemical properties of the phenol resin described by Mr. Aylsworth correspond minutely to every prior description of these so-called fusible soluble resinous condensation products.

The Baekeland Belgian and French patents, as well as the corresponding Hungarian patent, mention the use of a phenol-alcohol, or its equivalents, heated in presence of formaldehyde or its equivalents. The phenol-resin described by Mr. Aylsworth is an equivalent of phenol-alcohol, as conclusively shown by DeLaire (see Eng. patent No. 15,517, 1905, and D. R. P. No. 189,262, 1905).

The dishydration of phenol-alcohol produces fusible phenol-resins, specially if a slight excess of phenol is present.

In the process described in Mr. Aylsworth's patent, hexamethylenetetramin is used instead of formaldehyde, but this hexamethylenetetramin is a well-known equivalent for formaldehyde, or better for a mixture of formaldehyde and ammonia. Whenever ammonia and formaldehyde are mixed together, hexamethylenetetramin is produced forthwith. So practically, whether you make a mixture of phenol and add formaldehyde, and then add ammonia, or whether you add ammonia to the formaldehyde first, or to the phenol first, and then afterwards add the formaldehyde, the mixture behaves entirely as if an equivalent amount of hexamethylenetetramin were used. This fact is in direct contradiction with the statement contained in Mr. Aylsworth's description, that no accelerating or condensing agent is used; indeed, the formaldehyde and the condensing agent, ammonia, are used here at the same time. In the Baekeland U. S. patent No. 942,809, ammonia is used as an accelerating or condensing agent, and it is expressly stated that the addition of the ammonia can be made at any stage of the reaction. As a further contradiction to the claim in the Aylsworth patent that no condensing agents are used there, it should be pointed out that a little further in the text, he mentions the use of amids of weak organic acids. But the value of these products as condensing agents has been disclosed in Baekeland's U. S. Pat. No. 942,809, in the text whereof it is stated that ammonia can be replaced by amines and amids of weak acids (see also Eng. Pat., Baekeland, No. 21,566, 1908).

Special stress is laid in the Aylsworth patent on the addition of substances which make, with the final product, a so-called solid solution, thereby increasing plasticity. This claim to novelty is also anticipated in some of my pending patents which have been filed at a date decidedly prior to Mr. Aylsworth's applications.

A special reference is made to the fact that in the Aylsworth process, the use of pressure can be dispensed with. In most of the processes described and patented by me, the use of pressure is only resorted to in special conditions in order to accelerate or expedite the process, but in many cases, is entirely dispensed with. Indeed, the use of small quantities of basic or alkaline condensing agents, which I was the

¹ Loc. cit.

first to publish and patent, enables to obtain rapid hardening at relatively moderate temperatures, which can be rapidly increased without the intervention of pressure. Nevertheless the process will be quicker and much more practical if at once the maximum temperature be applied and then, of course, pressure shows its strikingly favorable action. This pressure can then be applied in a hot hydraulic press or in a bakelizer, or any convenient way.

L. H. BAEKELAND.

YONKERS-ON-HUDSON, JUNE 12, 1911.

GEMS THAT RESEMBLE THE DIAMOND.

In spite of many seductive advertisements there is no gem that "looks just like a diamond." Nor should we expect to find one, for, while two different substances may have a number of properties in common yet a study of *all* the properties of each will show many which differ. Still there are a number of gems which possess to a considerable degree some of the properties of the diamond and when well cut these gems can deceive and frequently have deceived those not expert in the determination of precious stones.

In times past such gems have even passed current as diamonds before the scrutiny of experts, for until the general spread of science, such tests as those of specific gravity, refraction, etc., were not applied, and many colorless zircons, topazes and sapphires probably passed as rather inferior diamonds. It is even claimed that the Braganza, a mammoth uncut gem among the Portuguese crown jewels, is merely a fine specimen of colorless Brazilian topaz, yet it has been listed for years among the world's greatest diamonds.

Among the gems which may be regarded as so closely resembling diamond as to be likely to deceive the inexpert, I will list and briefly discuss the following:

First, the colorless or pale zircon, sometimes called in the trade, the jargon;

Second, the colorless sapphire;

Third, the colorless true topaz;

Fourth, the colorless beryl;

Fifth, colorless phenacite;

Sixth, colorless quartz.

These and a few other and rarer colorless gems constitute the list of gems that resemble the diamond. I may say at this point that none of them resemble the diamond to the casual glance so closely as does the very brilliant lead glass used in making the so-called "paste" or "strass" imitations so widely advertised and sold under various fictitious titles in many cities. This artificial material possesses a very high refractive index and is capable of separating the various colors of the spectrum so widely that it affords a brilliancy and "play" of colors that nothing but the diamond can equal. It is, however, deficient in hardness, being easily attacked by a file and consequently it does not long resist dulling and scratching from wear and hence does not hold its brilliancy. It is also easily attacked chemically by a number of things, with which it is likely to come in contact in wear and thus be still further dull. In many of the imitation diamonds the

tendency to scratch is partially prevented by using a thin slice of some hard gem material for the upper surface, making in other words a so-called "diamond doublet." This artificial gem has no real diamond about it of course, although formerly a few real diamond doublets were made in which the upper half of the stone was made of real diamond and the lower half of some less costly white gem, the two being joined at the girdle by means of gum mastic or other transparent cement. The modern diamond doublet usually has an upper surface made of a very thin slice of garnet, covering usually only the table, as the part subject to greatest wear. The garnet used is pale in color and so thin is the slice that hardly any color is visible. The remainder of the "stone" is entirely of lead glass. Some of these "works of art" are certainly very beautiful and at a reasonable distance they would probably puzzle an expert.

While none of the genuine gems I have listed quite approaches the "paste diamond" in play of colors, many of them are nearly as brilliant in the lively play of white light which they afford when cut in a manner suited to such material, which cutting, by the way, should not be just like that most suited to the diamond.

In regard to the order of precedence among them, I should put the colorless zircon first. This gem possesses adamantine luster in a high degree, that is, the amount of light reflected from its *top* surfaces, when properly inclined to the light, approaches closely to the amount reflected by a genuine diamond surface. This effect must not be confused with the brilliancy of the flashes of light reflected from the *interior rear* surfaces of the stone. That is another matter. This adamantine luster gives what the French call *éclat* to the zircon. It is snappy, cold and glittering in its luster. So closely does it resemble diamond in this respect that I was able to deceive a diamond cutter in one of the best establishments in this country by a brown zircon which I wore in my scarf this summer. He referred to it as my "brown diamond" although he was not above four feet away and looking squarely at it. Of course in a stone of positive color, no large amount of prismatic "play" is possible or expected, and so the lack of it in my brown zircon was not felt. The cutter would doubtless have detected the difference in a colorless zircon but one not so expert might not.

Of course, in hardness, in specific gravity and in refraction, the zircon is not like the diamond. It is much softer being only 7.5 as against 10 in hardness by Moh's scale; its specific gravity is 4.4-4.7 as against 3.5-3.6 for diamond; and it is doubly refracting while diamond is singly refracting. It could thus be readily distinguished by any one who understood the application of the tests for the above properties.

After the zircon in order of excellency I would place the white sapphire. Its index of refraction is higher than that of any of the other gems in my list except the zircon, and its great hardness renders it capable of taking and holding a polish almost equal to that of the diamond. It does not possess the adamantine luster, however, its luster is probably best defined

as splendid. It exceeds the luster of glass and of the other gems in my list which have what is usually styled the vitreous luster. Both the zircon and sapphire when well cut and pure white show a faint "play" of colors and both give fine brilliancy in their reflections of white light. I have fooled many retail jewelers with a fine specimen of white sapphire which I have set in a ring. As in the case of zircon, so with the sapphire, a test of its hardness, specific gravity and refraction will at once serve to distinguish it clearly from diamond. Its hardness is 9, its specific gravity 3.9-4.1 and it is doubly refracting.

Next to the zircon and sapphire I would place the white topaz. It gives a faint play of color, is hard enough to resist wear for years and takes an extremely high polish. Many so-called "white topazes" advertised by unscrupulous dealers are only lead glass, and many more are cut from the softer and cheaper rock crystal. I had one of the latter sent me recently under a guarantee that it was a genuine white topaz. It was a finely cut and very brilliant gem but it was *not real topaz*. I sent it back after a specific gravity test, which I recorded on the inside of the paper in which the gem was wrapped, saying that I was sorry but I couldn't use "that kind."

I have already referred to the Portuguese "Braganza" as probably a white topaz. The fact that the specific gravity of topaz is very nearly that of diamond makes it a still more dangerous imitator, but its hardness of 8 and its double refraction serve to distinguish it.

The other colorless gems in my list, phenacite, beryl and rock crystal very closely resemble each other and all give brilliant stones when properly cut. The phenacite and beryl are but slightly softer than topaz and would wear well. The rock crystal is the softest in my list, and while it will hold its brilliancy for some time it would dull in the course of a few years or even months if subjected to hard wear as a ring stone.

Aside from the peculiar interest which attaches to these colorless stones from the fact that they may be and doubtless many times in the past have been substituted for diamond either ignorantly or with purpose to deceive, there is, I believe, a worthy interest in them for what they really are and for the real beauty which they undoubtedly possess.

When men shall have learned to practice honesty as the best policy, it is to be hoped that these gems, which do truly somewhat resemble the diamond, but which resemble each other more, may come into their own and be appreciated and valued for their own beautiful qualities.

COMMERCIAL TURPENTINES OF UNITED STATES.¹

The turpentine-producing area in this country is practically confined to the coastal plains region of the Southern States. In the earlier days the industry was best developed in North Carolina, but owing to destructive methods of turpentine orcharding, in conjunction with lumbering, fires, etc., the industry has gradually worked southward and westward, until at

present Florida produces the most turpentine, followed by Georgia, Alabama, Mississippi, Louisiana, North Carolina, South Carolina, and Texas, in the order named. The statistics of production in various years from 1870, taken from the census reports, are given in the following table:

Year.	Gallons.	Value.
1870.....	6,004,887	\$ 2,194,498
1880.....	17,565,250	1,542,120
1890.....	17,316,200	5,459,115
1900.....	38,488,170	\$14,960,235
1905.....	30,687,051	15,170,499
1908.....	36,589,000	14,112,400

It is the trade practice to grade turpentine according to its color, and the various grades are known as "water white," "standard," "off one shade," "off two shades," and "off three shades." The latter is not merchantable. Under the trade regulations the deductions in price on turpentine off one shade is 2.5 cents per gallon and off two shades 4 cents per gallon.

About half of the turpentine produced in this country each year is exported, chiefly to Europe, while by far the larger part of the remainder is consumed in the varnish and paint industries, and small quantities are used in medicine and as a solvent for gums, rubber, fat, and waxes in this country. No statistics are obtainable showing the quantities consumed for the latter purposes, nor in thinning paints and varnishes at the time they are actually used. The distribution of turpentine produced in 1905 was as follows:

	Gallons.
Produced.....	30,687,051
Exported.....	15,894,813
Used in manufacture of paints and varnishes...	7,160,774
Used in other industries (by difference).....	7,631,464

The turpentine found on the American market is quite frequently adulterated with cheaper and inferior oils, those most commonly employed being the petroleum oils having specific gravities corresponding closely to that of turpentine, and distilling at about the same temperature. Other adulterants are certain coal-tar oils, rosin spirits, and wood turpentine, which closely resemble turpentine in specific gravity, distilling temperature, and some other properties.

It is quite common for druggists, both wholesale and retail, to buy turpentine from oil and paint dealers or from any one handling it in large quantities, and, therefore, samples have been secured from oil and paint dealers, as well as from druggists, their stock being in many instances representative of the turpentine sold at the drug stores in the same community. In fact rarely is any distinction made between turpentines for drug or technical purposes.

Though it is known that spirits of turpentine is very frequently adulterated, no systematic investigation of the subject in this country is on record. For this reason, the results obtained on samples collected from all parts of the country are recorded for the information of the public, to show the extent of the practice of adulteration, and to furnish more complete data for the grading of American turpentine and the preparation of specifications therefor which shall be

¹ Abstract from monograph prepared in Bureau of Chemistry, Department of Agriculture, by F. P. Veitch assisted by M. G. Donk.

fair to the producer and also insure that the consumer secures the article for which he pays.

Straight wood turpentine are readily distinguished from gum turpentine by their odor, or when they have been very carefully refined, by the odor of the first fraction, or of the residue from fractional distillation. One or both of these portions have the peculiar "sawmill smell," and the residue has a camphoric and somewhat nauseating odor characteristic of wood turpentine, which is quite different from the mild, sweet fragrance of gum turpentine.

Destructively distilled wood turpentine and also rosin spirits are more readily distinguished from gum spirits by their odor than is wood turpentine prepared by steam distillation, and they also give distinguishing color reactions when mixed with sulphurous acid as suggested by Hertzfeld or with hydrochloric acid.

Turpentine adulterated with more than 10-20 per cent. of coal-tar oils, or of gasoline or kerosene which have not been deodorized, may usually be readily detected by the characteristic odor of the mixture. The odor of rosin spirits, while quite distinctive, is difficult to detect in mixtures with turpentine. The presence of petroleum oils is also indicated by bubbles or "beads" persisting for a few moments on the surface of the turpentine shaken in a partly filled bottle.

The presence of more than about 10 per cent. of kerosene or similar mineral oils is readily detected by the spot which a few drops of the sample placed on white paper leaves on drying. Gasoline and other light mineral oils do not leave this spot.

The detection of mineral oils in turpentine is relatively quite simple, and is accomplished by mixing the turpentine with a certain proportion of sulphuric acid of a given strength, in which the turpentine is destroyed and mixes with the acid while most of the mineral oil remains unaffected and separates in a layer on top of the acid.

Only a few of the samples taken of producers' goods are adulterated with mineral oils, while the turpentine of the primary buyers and dealers in the turpentine belt is adulterated extensively, showing 13.6 and 18 per cent. of adulterated samples, respectively. The dealers' samples contain a much higher percentage of the adulterant than either of the other two classes, exceeding the producers' goods by 3.5 and the primary buyers' goods by 4.2 per cent. Adulterations occur more frequently and are present in larger quantities outside the turpentine-producing belt than within it. Eighteen per cent. of all the samples collected were adulterated, and the average percentage of adulterant in these was 6.1 per cent., ranging from 1-71 per cent. in the individual samples. The average amount of mineral oil in a barrel of the adulterated samples was approximately 3 gallons, which, basing the calculation simply on the cost of the two materials, made these adulterated turpentine worth fully \$1.50 less per barrel than unadulterated stock. These facts assume graver significance when it is remembered that turpentine is an article so well known and so generally used that it is carried in stock and sold by merchants

generally, particularly by country merchants, and when bought from any source is liable to be employed indiscriminately, either medicinally or technically.

The consumption of turpentine in the United States during 1908 was approximately 15,000,000 gallons. If 18 per cent. of this was adulterated, then approximately 3,000,000 gallons of adulterated turpentine, containing an average of at least 6 gallons per hundred of mineral oil, costing about one-fifth as much as the turpentine, was sold at turpentine prices.

CYANAMID IN AMERICA.

There are now twelve factories engaged in the manufacture of cyanamid (lime nitrogen), and one or two others in the course of construction with an aggregate present and projected capacity of about 250,000 tons. These factories are scattered throughout Europe with the exception of the American Cyanamid Company which is located at Niagara Falls, Ontario. The American Company which has been operating since January, 1910, now has a capacity of approximately 13,000 tons a year. The product is somewhat more highly developed than much that is produced abroad, due to the requirements of the American market—that it shall be capable of being compounded into complete fertilizers. The free lime which constitutes a considerable percentage of "Cyanamid" is hydrated, and it also undergoes a further treatment to eliminate to a large extent the dust nuisance which was so objectionable in the original product.

The plant at Niagara Falls is of a most substantial character, the buildings being entirely of concrete and steel even to the roofs. Power is the chief single item of expense, and as the factory runs every minute of the day, 365 days in the year, it must be had continuously and cheaply. The process as followed by the American Cyanamid Company consists of the making of calcium carbide, which is pulverized and treated in electric ovens to nitrogen gas under pressure. The nitrogen gas is derived from the atmosphere, being a modification of the well-known copper process. The American Cyanamid Company is, with one or two exceptions, the only cyanamid factory which does not use the liquid air process for the manufacture of its nitrogen.

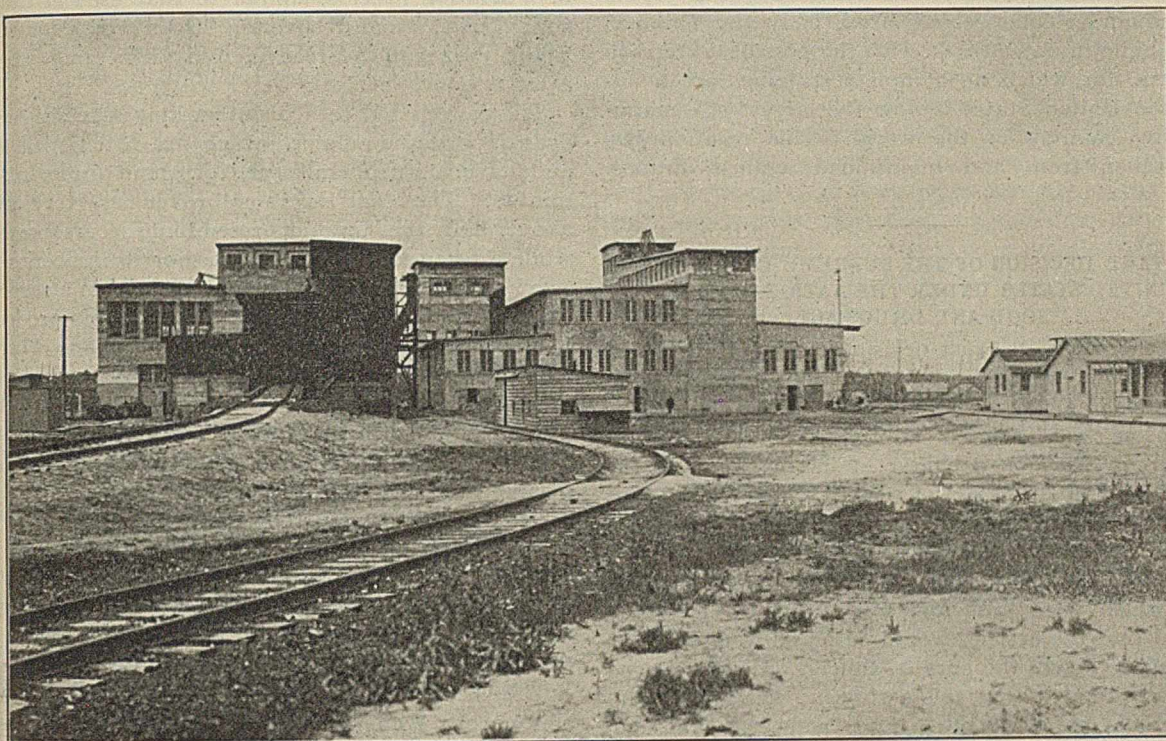
The price per unit of ammonia at Baltimore, the chief distributing point, was fixed early in the past season at 20 to 25 per cent. in excess of the ruling price for sulphate of ammonia and has been maintained at that figure. If cyanamid can eventually be sold at prices materially cheaper than other nitrogenous fertilizers, its utilization on a very large scale would appear extremely probable.

As yet, we have very little data from field tests in this country to determine the efficiency of cyanamid as a crop-producer as compared with other nitrogenous fertilizers, but the agricultural departments of Europe have done considerable work along this line during the past four or five years, and the results have for the most part been very favorable.

The comparative efficiency of nitrogenous fertilizers is affected by the nature of the soil and the

character of the season, and in the tests made the results obtained vary considerably. It is only by careful experiment that it can be definitely known which fertilizer is likely to be most profitable for a certain soil. Cyanamid has not been used as a fertilizer but for only a comparatively short time, and further

The imports of silk goods for the same period show a variation from year to year but no increase in the last 30 years. The average for that term has been about \$32,000,000 a year, the average for the period 1880-'89 being \$33,000,000. Thus on a basis of factory and import prices the per capita expenditure in 1880 was



experiment and utilization are necessary to establish its relative merits as compared with other nitrogenous fertilizers. The reports of experts, however, who have experimented in European countries with cyanamid agree to its value, and it would appear that in certain soils it produces as good, if not better, results than other nitrogen-yielding fertilizers.

Cyanamid contains about 60 per cent. of lime, and like nitrate of calcium is especially adapted to soils deficient in that element. Its action is less rapid than that of nitrate of soda, but is continuous and lasts longer. One hundred and sixty American fertilizer companies are now using the product made at Niagara Falls as a source of nitrogen in their complete fertilizers.

SILK INDUSTRY INCREASED \$90,000,000 IN TEN YEARS.

In a bulletin issued by the Bureau of the Census the statement is made that "the development of the silk industry of the United States during the last few years is one of the most interesting features of the country's progress." Reference to the records of the trade shows the product value of the industry for the years indicated as:

1869.....	\$ 12,210,000
1879.....	41,033,000
1889.....	87,298,000
1899.....	107,256,000
1904.....	133,288,000
1909.....	196,425,000

\$1.45 and in 1909 it was \$2.50. The greatest gain in the last 10 years has been made in the output of dress goods, which in 1909 represented 55 per cent. of the entire product value. Ribbons represented 17 per cent. of the total value, velvet and plushes 7 per cent., and laces, braid and trimmings 5 per cent. The output value of dress goods doubled in 10 years.

It appears that the product value of the 186,000,000 yards of dress goods made in 1909 averaged 58 cents a yard, while the value of the 88,000,000 yards made in 1899 was 60 cents. The supply of animal silk has more than doubled in the last 20 years, and the price of the commodity shows little or no increase in that time; yet so sharply has demand followed supply that, as stated by the Bureau of the Census in an earlier report, "ingenious efforts have been made to discover a substitute for the animal product, and the manufacture of artificial silk is assuming considerable importance." At present the chemically made substitutes are used chiefly in the manufacture of braids and trimmings.

Of the 843 silk mills of the country, 347 are located in New Jersey, 219 in Pennsylvania, 168 in New York, 47 in Connecticut, 19 in Massachusetts, and 13 in Rhode Island, leaving only 30 located elsewhere. The New Jersey product is valued at \$65,000,000, that of Pennsylvania at \$62,000,000, of New York at \$26,500,000, of Connecticut at \$21,000,000, thus making for those states 95 per cent. of the entire product.

Massachusetts produces a little less than 5 per cent. The notable increase in the industry in the last 10 years has been in New Jersey and Pennsylvania where, on a basis of product value, the honors are about equally divided. Imports of raw silk, admitted free of duty, are valued at about \$75,000,000 a year, nearly 60 per cent. of the total being bought in Japan. The remainder comes chiefly from Italy and China.

The bulletin notes that "with the possible exception of China, for which no complete statistics are available, the United States is now the largest silk manufacturing country in the world. This position has been taken from and maintained against France, since 1905."

IMPORTANT DECISION OF THE SUPREME COURT OF THE UNITED STATES UNDER THE NATIONAL PURE FOOD AND DRUGS ACT.

Together with its trust decision the Supreme Court handed down, on May 29th, a most important decision in the case of Dr. O. A. Johnson, of Kansas City, Mo.

Johnson was indicted in the Federal courts of Missouri in 1909 on a charge of having violated the Pure Food and Drugs Act of 1906. It was alleged that Johnson, doing business under the name of a company, shipped from one State to another certain articles designated as "cancerine tablets," etc., the labels upon which were false and misleading in that they implied that the articles would cure and were effective in bringing about the cure of cancer. It was alleged in the indictment that this statement was untrue and the articles were worthless and ineffective for such purposes.

The Supreme Court decided that provided there is no misstatement on the bottle or package as to its contents, the manufacturer is free to sell his goods. Justice Holmes announced the majority opinion, Justice Hughes delivering a dissenting opinion in which Justices Harlan and Day concurred.

The court acknowledged that "in a certain sense the statement on the label was false, or, at least, misleading," but it held that the language of the pure food law is such that the statement contained therein as to the meaning of misbranding "is aimed not at all possible false statements, but only at such as determine the identity of the article, possibly including its strength, quality and purity."

If a label were to state that the contents of a bottle was water when as a matter of fact it was other than water, it would come under the misbranding in the meaning of the law, according to to-day's opinion. But the opinion adds that when the statement on the box or bottle of medicine is "shown to be false only in its commendatory and prophetic aspect," it did not come within the act.

This decision appears to be of importance for the patent medicine business in the United States and is a defeat for the government officials in charge of the National Pure Food and Drugs Act who always claimed that labels must not bear any inferences as to "cures," etc., because such claims were misleading and false.

A NEW CANE SUGAR PROCESS.

A new process of sugar-making is being tried by one of the large sugar companies in Cuba. In the ordinary process the juice is extracted from the cane by pressing it between sets of rollers. In the new process the cane is broken up, dried and finally treated by a diffusion or a solution process, similar to that used in treating sugar beets, which recovers a larger proportion of the juices than can be recovered by squeezing between rolls.

The cane is fed to a disintegrating machine having drums, 4 feet diameter, which are fitted with teeth and have a peripheral speed of about 6,500 feet per minute. The cane is thus broken up very small, about half the product resembling coarse sawdust while the remainder consists of short thin fibers. The two kinds of material may be separated in a revolving screen or may be handled together. This product is fed by force-feed rollers into drying kilns where it travels back and forth on conveyor belts running in opposite directions. These belts are staggered about 18 inches and the material from each belt falls to a lower one running in the reverse direction. Air heated to about 190° by exhaust-steam radiators is admitted to the kilns and is further heated to 240 or 250° by means of live-steam coils. The feed of material into the kiln and the speed of the belts in the kiln are under the control of the operator, who also controls the admission of exhaust steam to the radiators and live steam to the superheating coils.

The dried material is discharged from the lowest belt onto a transverse elevating conveyor which delivers it to a compress or baler; the bales are about 14 × 18 × 36 inches, with a density of about 50 lbs. per cubic feet. The material can then be stored or sent direct to the refinery, where the sugar is extracted by the diffusion process. The pulp remaining contains but a very small proportion of sugar (only a fraction of 1 per cent.) and it is suitable for paper-making with much less cooking than is required with ordinary material. The process is the invention of Mr. Geo. W. McMullen, of Chicago, and the first plant is now in experimental use at a mill of the Nipe Bay Co. The machinery was built by Roberts Brothers, of Chicago.

Under the ordinary roller process the cane is fed in layers, 6 or 8 inches thick, to a set of three large rolls (two lower and one above); these crush and compress the cane and expel the juice. The crushed cane then goes to a second set of rolls and more juice is expelled, but after all the rolling the crushed waste material or "bagasse" contains a considerable proportion of sugar (from 15-30 per cent.). Much of the bagasse is fed to the furnaces, but is so wet that a considerable amount of wood is required to make it effective as fuel.—*Engineering News.*

RADIOACTIVE INVESTIGATIONS IN RUSSIA.

Special Correspondent.

Although Russia is rich in mineralogy embracing a number of the known rarer metals, it is generally deplored among Russian scientists that in that country

practically nothing has been done to meet the demand that has arisen for minerals of a radioactive nature. Therefore the Imperial Russian Technical Society may be congratulated on such steps as it has taken towards the study of radioactivity. It is even stated in a report on the Odessa laboratory, which has been specially established for the purpose of investigating supposed radioactive minerals, that no deposit of ore has been discovered in the country of a radioactive nature and even the mineral water wells have not been investigated.

On the initiative, however, of E. S. Burksler, the Odessa section of the Society proposed to establish a laboratory for the specific object of investigating the radioactive minerals of Russian springs and earths and particularly those of the estuary on which Odessa is situated. In a land so rich in open mines as Russia it is impossible to assume the absence of radioactive minerals and therefore the radioactive laboratory appealed to mining engineers, to the Geological Committee and others to send on to it for investigation, which it would conduct free of charge, minerals and ores in which the presence of uranium or thorium might even be only suspected. For guidance in the investigations a table of uranium and thorium ores has been issued translated from the French. In order to insure an efficient equipment of a laboratory the Technical Society sent the manager of the laboratory, Mr. E. S. Burksler, to France and Germany to learn the technique of radiological investigation. At the present moment the necessary apparatus is being installed for the investigation of radioactive earths, water, and powerful radioactive substances, and investigators are already examining the mud and the water of the Odessa estuary. In November, 1910, Mr. E. S. Burksler made a statement of the chemical section, of the results of his investigations into the radioactivity of the town supply water.

On the suggestion of institutions and private persons the laboratory will investigate the radioactivity of various substances at a fixed tariff (presumably this has reference simply to those persons seeking information for commercial purposes). The tariff of radiological investigation for water in Maxe units is 15 roubles for muds; and for earths 7 r.; for determining emanations proceeding from mud or earth, from 20-50 r.; and for determining the radioactivity of minerals or radioactive medicines (not lower than 0.1 uranium units for medicines) in uranium units, 7 r. It may be added that the Imperial Russian Technical Society also has a technico-chemical laboratory in St. Petersburg for scientific and industrial purposes. But the Odessa institution appears to be the only one founded and equipped for the specific purpose of investigating the radioactive resources of Russia.

RUBIDIUM AND CAESIUM FELDSPARS.

Special Correspondent.

An interesting note was presented to the St. Petersburg Academy on 23rd March/5th April on rubidium and caesium feldspars by V. I. Vernadsky. He states that "the unexpected cessation of my pro-

fessional work in the Moscow University forced me to abandon several experiments at quite a incompleting stage. Among these experiments I should like to observe my initial work on the synthesis of rubidium and caesium orthoclases because I note that in this direction other work is being done. The effort to synthesize $Rb_2Al_2Si_6O_{18}$ and $Cs_2Al_2Si_6O_{18}$ were begun by me in view of the following considerations: caesium and rubidium are widely distributed in feldspars. (Regarding this distribution see V. Vernadsky's works in the Geological Museum of the St. Petersburg Academy, 1908, page 88; also his notice to the Academy of Science, St. Petersburg, 1909, pages 163 and 822.¹ In this article the book references are given.) It must be supposed that they are found in the formation of isomorphic mixtures corresponding in composition to potassic feldspar (orthoclases and microclines), that is, we have here a body of the type $(K, Rb.Cs)_2Al_2Si_6O_{18}$. As is known orthoclases generally after fusion do not yield crystals, but the fusion possesses a glassy composition. One may therefore suppose that the crystallization of this body is assisted by the presence of caesium and rubidium, while it would be interesting to investigate the caesium and rubidium orthoclases also for the explanation of the causes of the variations in the properties of orthoclases, which do not result from the presence in the isomorphic mixtures of sodium and calcium-alumosilicates to be found in them.

"My preliminary experiments made with the addition of rubidium (either in the form of Rb_2CO_3) to the orthoclase testify to the favorable influences of these bodies on the crystallization of orthoclase. The fusion of rubidium corresponding to the theoretical composition (of $Al_2O_3SiO_2Rb_2CO_3$) also appears crystalline. Unfortunately I was not able to make more particular investigations on this point. The experiments of caesium were only begun, and definite results were not obtained, but apparently caesium acts similarly to rubidium."

HYDROXIDE OF CHROME TO BE ADMITTED DUTY-FREE.

The United States Court of Customs Appeals, the highest instance in tariff matters, rendered a decision on June 2nd, in which the Board of General Appraisers' opinion on the classification of hydroxide of chrome was affirmed; as a result this material will be placed on the free list under Section 499 of the Act of 1909, as an article in a crude state used in dyeing and tanning.

The importers claimed that this substance which is won as a by-product in the manufacture of anthraquinone from anthracene by means of oxidation with bichromate of soda in sulphuric acid solution was not a chemical compound to be assessed for duty at 25 per cent. *ad valorem*, but an article in a crude state used in dyeing and tanning.

The court held that the article as imported is certainly in a crude state in two respects: First, the article itself is in the state of its first production,

¹W. Vernadsky and E. Revovsky in the *Comptes Rendus de l'Acad. d. Soc. de Paris*, December 27, 1910.

without being refined by additional treatment applied for that purpose. In this condition it is mixed with various impurities. This is worthy of notice, although it may not be the controlling consideration with the purview of paragraph 499. The filtering and washing process described in the testimony had no effect on the article itself, other than "to get it by itself."

Second, it is an article in a crude state within the meaning of the paragraph because as imported it is not in a condition fit for use in dyeing or tanning, but it is only a raw material which is to be converted by further treatment into other articles fit for such use. This is the important aspect in which the article may be said to be in a crude state. The paragraph treats of materials which are used in dyeing and tanning.

The importation is simply a raw material in its relation to those uses and is therefore in a crude state in that respect. To prepare it for such uses other chemical elements must first be added to it, so that when finally used for such purposes it presents a different chemical combination.

The court finds that this substance is used in this country as a mordant in the printing of textile fabrics and in tanning. In neither case, however, it is claimed, is it used in the form in which it is imported. For use in tanning it is treated with sulphuric acid, forming a sulphate of chrome. In all its uses it appears that the article imported has to be converted chemically into new and different combinations.

THE ORIGIN OF HYDROCARBONS.

In Bulletin 401 of the United States Geological Survey, entitled "Relations between Local Magnetic Disturbances and the Genesis of Petroleum," by George F. Becker, the condition of knowledge with reference to the origin of petroleum and other bituminous substances is reviewed. Some oils, says Mr. Becker, are undoubtedly organic and some are beyond question inorganic. They may have been derived from carbonaceous matter of vegetable or animal origin, and they may have been derived from carbides of iron or other metals. It is also barely possible that the hydrocarbons exist as such in the mass of the earth.

While studying the subject, Mr. Becker was led to inquire whether any relation could be detected between the behavior of the compass needle and the distribution of hydrocarbons. Not much could be expected from a comparison of these phenomena, for magnetite exerts an attraction on the needle whether this ore occurs in solid masses or is disseminated in massive rocks; moreover, many volcanic rocks possess polarity. In glancing over a map of the magnetic declination in the United States Mr. Becker found that the irregularities of the curves of equal declination of the compass were strongly marked in the principal oil regions. The most marked agreement is found through the great Appalachian oil field, which is the area of greatest variation in declination. In California, also, strong deflections accompany the chain of hydrocarbon deposits.

These observations are to some extent also supported by conditions in the Caucasus, where great magnetic disturbances exist. While the theory of the inorganic origin of the hydrocarbons as exploited by various scientists is not proved by this study, yet the contention that great oil deposits are generated from iron carbides is strongly borne out by a study of the map of magnetic disturbances in the United States. The map shows that petroleum is intimately associated with magnetic disturbances similar to those arising from the neighborhood of substances possessing sensible magnetic properties, such as iron, nickel, cobalt, and magnetite.

VANADIUMISM.

Dr. Walton Forest Dutton, of Carnegie, Pa., describes in *The Journal of the American Medical Association*, June 3, 1911, under the above name, a new industrial disease of interest to chemists, caused by the exposure to dust and fumes of the various vanadium compounds, especially vanadium trioxid.

Vanadiumism is a chronic intoxication, of which the symptoms are emaciation, an anemia not altogether unlike chlorosis, a dry irritating paroxysmal cough, sometimes so intense that hemorrhages result, irritation of the nose, throat and eyes, gastro-intestinal involvement demonstrated by nausea and diarrhea, followed by obstinate constipation. Albumin, casts and blood are often present in the urine.

In the absence of grave, renal, blood, nervous and lung involvement, the prognosis is good, but where there is active inflammation of the kidneys and lungs it is unfavorable. Dr. Dutton states that the prevention of vanadiumism is difficult in vanadium works, owing to the carelessness of employees and employers. Means to allay and carry off the dust and fumes should be employed constantly. Perfect ventilation and the use of respirators are imperative. The nasal and oral cavities should be thoroughly cleansed with some efficient alkaline spray, such as the ordinary Dobell solution, followed by a mentholated oil spray. The stomach should be washed out, and later the intestines freely evacuated with a saline laxative. The cough may be allayed by giving terpin hydrate $\frac{1}{4}$ grain, heroin $\frac{1}{8}$ grain, and creosote $\frac{1}{2}$ minim, every two hours with counter-irritations of iodine or mustard applications over the chest. The inhalation of stimulating vapors is salutary. Iron, calisaya, and strychnin will meet the needs of anemic, nervous and debilitated conditions. Codliver oil may be given with advantage. Active outdoor exercises are essential. Turkish, Russian or cabinet baths may be given to aid elimination.

ADRENALIN AND A NEW MEMBER OF THE "DIGITALIS SERIES."

One of the most interesting investigations of modern times has just been carried out and published in the May 27, 1911, number of *The Journal of the American Medical Association* by John J. Abel and David I. Macht, of Johns Hopkins.

In examining the convulsant action of certain organic dyestuffs, the authors had the opportunity of trying the effect of these substances on a tropical toad, *Bufo Agua*. Scraping off some of the milky secretion which exudes from the parotid gland of the animal with an iron knife, the authors noted a bluish green discoloration on the blade. This observation led them to test the diluted secretion with ferric chloride, whereupon the characteristic green color of the pyrocatechin reaction was developed. As this reaction is given by the active principle of the suprarenal glands it was soon demonstrated that the secretion contained a substance identical with epinephrin (adrenalin).

Quantitative experiments showed that the secretion contained rather large amounts of this substance (0.3 per cent. in the suprarenal glands of beeves and about 5 per cent. in the secretion) and since the secretion is obtained by squeezing (or milking) the parotid gland, it is not at all impossible that this toad may be utilized in the future for furnishing the raw material for the production of adrenalin.

Associated with adrenalin in the venom of the toad is a digitalis-like substance, to the presence of which the secretion of the toad owes its efficacy as an arrow poison. The authors call this new material "Bufagin" and give it the formula $C_9H_{12}O_2$.

If the content of adrenalin is 5 per cent. in the secretion, bufagin occurs in it to the amount of 36 per cent. Pharmacological experiments showed that bufagin is one of the most effective members of the digitalis series.

The toads which were experimented upon were obtained from the neighborhood of Montego Bay, Jamaica, where they are popularly known as bullfrogs.

A PRACTICAL MANUFACTURER ON THE SYNTHESIS OF RUBBER.

In the May number of the new journal *Kunststoffe*, Dr. Gerlach-Hannover, a practical rubber manufacturer, makes the following statement:

"The problem of producing caoutchouc synthetically has been solved. But just as in the case of indigo, 20 years lapsed before the synthetic product was successfully launched, it will take at least 20 years before synthetic rubber will make its appearance commercially. It will take perhaps longer with caoutchouc because the physical properties of this material are not as well known as those of indigo. The high price of the natural product, stimulated research and after the pioneering experiments of Harries, the Elberfeld Farbenfabriken have finally succeeded in producing larger quantities of a product derived from a material closely related to isopren. At this stage of the development it was found out that there exist many sorts of rubber which are near relatives, but still possess different characteristics.

"The first synthetic caoutchouc which was placed at my disposal, for example, did not unite with sulphur and had a leathery appearance. This was not to be wondered at, as there are known some varieties of natural caoutchouc which cannot be vulcanized.

Soon another sort of rubber came to my notice which showed better affinity for sulphur, but still could not be perfectly vulcanized. Above all it lacked elasticity. Soon, however, larger quantities of a third sort were submitted to me which to my great astonishment showed all the excellent properties of natural rubber.

"But now the question arises whether this material of the Elberfelder can be economically produced on a large scale and may thus become a danger for natural rubber. It cannot be denied that the substance, which possesses good qualities, can be utilized for practical purposes. Its price is not high but it is a complex question to decide whether this synthetical product will become a danger to natural rubber. All kinds of economical and commercial conditions must be taken into consideration. One thing, however, is certain, that synthetic rubber will soon be a commercial article."

WEARING AWAY OF MOTHER EARTH.

Investigations by the United States Geological Survey of the erosion of numerous drainage basins of the United States show that the surface of the country is being removed at the average rate of about an inch in 760 years. Though this amount seems trivial when spread over the surface of the country, it becomes stupendous when considered as a total, or even in separate drainage basins. Mississippi River, for instance, carries annually to the sea 136,400,000 tons of dissolved matter and 340,500,000 tons of suspended matter, and of this total Ohio River carries 83,350,000 tons and Missouri River contributes more than twice as much. Colorado River, which has built up for itself a vast delta, brings down more suspended matter than any other river in the United States, delivering annually 387 tons for each square mile of its drainage basin, or a total of 100,740,000 tons.

The rivers of the United States carry to tidewater every year 270,000,000 tons of dissolved matter and 513,000,000 tons of suspended matter. This total of 783,000,000 tons represents more than 350,000,000 cubic yards of rock, or 610,000,000 cubic yards of surface soil. If this erosive action had been concentrated on the Isthmus of Panama at the time of American occupation it would have excavated the prism for an 85-foot level canal in about 73 days.

GLASS MACHINE COMPANY INSOLVENT.

On May 18th involuntary bankruptcy proceedings were filed in the United States District Court at Pittsburg against the Colburn Machine Glass Co., on petition of The Star Glass Co., of Reynoldsville, Pa., The H. L. Dixon Co. and The Pittsburg Clay Pot. Co., of Pittsburg, and The Dover Fire Brick Co., of Cleveland, Ohio, whose aggregate claims amount to \$12,037.07.

These proceedings have to do with the sheet glass drawing process upon which the eyes of glass manufacturers throughout the world have been centered for upwards of a decade, which at various times has been

prematurely reported as having reached a stage of commercial success. While it is true that some window glass was manufactured by the process, the invention is still in an incomplete state and opinion is divided as regards the practicability of the idea. Some very competent authorities are still of the opinion that success could be wrested from failure if capital for continuing experiments could be obtained, while others look upon the proposition as a closed incident. The experimental plants at Franklin and at Reynoldsville were mechanical marvels which challenged the admiration of all who were privileged to witness their operation, but, as is indicated in this bankruptcy proceedings there was always something radically wrong which hundreds of thousands of dollars were unable to correct.

ACETPHENETIDIN LABELING DECISION.

In the case which the government had brought against the Antikamnia Co., the Supreme Court of the District of Columbia rendered a decision on May 29th, in favor of the Antikamnia Co. The question at issue was whether, under the National Pure Food and Drugs Act, the Antikamnia Co. was obliged to add on their label to the word of "Acetphenetidin" the legend "derivative of acetanilid."

The Antikamnia Co. prevailed against the government in their claim that the law does not require any such addition and that it was not the intent of Congress to demand that the name of the drug from whence it is derived should also be recited to properly label a headache powder.

It should be borne in mind that this decision was rendered in a demurrer case in which the fact that acetphenetidin was a derivative of acetanilid was technically conceded for the purpose of the arguments.

In reality, the Antikamnia Co., if unsuccessful in the demurrer, would have carried on the litigation on the theory that acetphenetidin is not a derivative of acetanilid and is not manufactured commercially from acetanilid and cannot be so produced unless acetanilid is first destroyed. In consequence of this decision, headache powders containing acetphenetidine need only bear on the label a statement of the quantity of acetphenetidine present.

"SOLIDIFIED" GASOLINE.

The *Automobile* states that this substance, the invention of a Roumanian chemist, Dr. V. Rosculetz, is the result of dissolving stearic acid (which has undergone prolonged treatment with hydrochloric acid at a high temperature) in the hydrocarbons to be solidified, the solution being mixed with an alcoholic solution of caustic soda at about 175° F. This mixture cools to a stiff, jelly-like mass, capable of being carried about and handled like any other solid body. Solidified gasoline is not a chemical combination, as the gasoline can be completely evaporated from it. Under the microscope it appears to have the structure of an extremely fine sponge, the pores of

which hold the gasoline in an unchanged form, the mass representing about 99 per cent. gasoline and 1 per cent. stearic acid and soda. The physical properties are the same as those of liquid gasoline, evaporation is easy, and the inflammability and carbureting power are very intense. Upon heating, it does not melt at ordinary pressures, but evaporates slowly; when ignited it burns like wood or coal, and the flame can be extinguished by water or by smothering with a cloth. It is stated that the volume of the solidified gasoline is from 10-20 per cent. less than that of the gasoline used in its preparation.

SILVER, COPPER, LEAD AND ZINC PRODUCED IN CENTRAL STATES IN 1909.

The final figures of the production of silver, copper, lead, and zinc in the Central States during 1909, compiled by C. E. Siebenthal and B. S. Butler, of the United States Geological Survey, have just been published and may be had on application to the Director of the Survey at Washington. The production by mines of these metals in Arkansas, Illinois, Iowa, Kansas, Missouri, Oklahoma, and Wisconsin is discussed by Mr. Siebenthal and that in Michigan by Mr. Butler.

The total production of the four metals in the States named in 1909 was \$63,992,548, as compared with \$56,326,703 in 1908. The production for 1907 was \$77,697,457.

The following table shows the values by States for 1908-9:

	1908.	1909.
Arkansas.....	\$ 58,130	\$ 57,144
Illinois.....	196,001	259,000
Iowa.....	41,414	6,876
Kansas.....	1,538,698	1,347,860
Kentucky.....	7,772
Michigan.....	29,601,603	30,586,693
Missouri.....	22,256,571	27,776,284
Oklahoma.....	575,330	1,137,770
Wisconsin.....	2,058,956	2,818,100
	\$56,326,703	\$63,997,999

EXPORT STATISTICS.

According to a statement of the Bureau of Statistics the fiscal year ending with the present month will show some remarkable records on the subject of exports and imports. The statement sets forth that for the first time in the history of the United States the export trade of this country this year will go beyond the \$2,000,000,000 mark.

The figures covering a period of 10 months furnish a basis for rough calculation of the trade for the full fiscal year. They suggest that the exports of raw cotton will aggregate not far from \$600,000,000 in value. Iron and steel manufacturers exported will approximate \$250,000,000; meat and dairy products, \$150,000,000; breadstuffs, \$125,000,000; copper, \$100,000,000; mineral oil, \$100,000,000; wood and manufactures thereof, \$90,000,000; and leather more than \$50,000,000.

The statement of cotton exported for 10 months shows a valuation of \$550,000,000, which is \$143-

000,000 greater than the corresponding months of 1910. This large value of raw cotton exported, which will be by far the largest total ever reported in any single year, is largely due, officials say, to high prices rather than to large quantities exported.

COMMERCIAL INVESTIGATION OF CHEMICAL INDUSTRY.

Owing to the increasing American interest in the chemical industry of the world, and the desire to secure information concerning its remarkable expansion in Europe, the Bureau of Manufactures is about to undertake a special investigation along these lines. Practical suggestions are invited from the trade as to the most desirable subjects to be taken up, and as to the most promising lines for commercial expansion. The imports of chemical goods and drugs into the United States are reaching enormous proportions, having been \$90,000,000 in value last year, against \$67,000,000 in 1908, while the exportations of chemical products from the United States have remained almost stationary, the aggregate reaching about \$20,000,000 per annum.

The chemical trade is a very broad one, but has special phases well worth study from the commercial aspect. To this end it is thought that correspondence as indicated will prove beneficial.

THE NOBEL PRIZE.

The Nobel prize for chemistry for the year 1910 has been awarded to Professor Wallach, the well-known authority on the essential oils and their constituents. On the occasion of the presentation of the prize Professor Wallach gave an address dealing with the progress of research in the domain of essential oil chemistry, and foreshadowed some prospects of the future development of the science. He urged that the aim of research work should be twofold: the exploitation of the latest synthetic methods, and their application to allied branches of chemical industry, especially in the synthesis of other compounds of similar structure and odor, and also the study of the conditions governing the formation of essential oils in the plant tissues.

ACETYLCELLULOSE FILMS WITHDRAWN FROM THE MARKET.

It appears that the Eastman Kodak Co. which, about two years ago, commenced the introduction of non-inflammable cinematograph films made from acetylcellulose has decided to abandon the manufacture of these films and to go back to the old film made from nitrocellulose. The acetyl films were inferior in lasting qualities to the old films and the general trade objected to their use.

It is claimed that newly invented appliances in the projecting machines will protect the nitro films against catching fire and exploding in case of accidents.

From a technical point of view it is greatly to be regretted that such a retrograde step becomes necessary.

ALASKA GOLD OUTPUT 1909.

In 1880 gold was produced in Alaska to the value of \$20,000. In 1909 the amount mined was valued at more than \$20,000,000. In 1888 silver was first produced in Alaska, to the value of \$2,181; in 1909 the value was \$76,934. In 1902 copper was first produced, to the value of \$41,400; in 1909 its value reached \$536,211. These and other statistics of production are shown by Alfred H. Brooks, of the United States Geological Survey, in "Gold, Silver, Copper, Lead and Zinc in the Western States and Territories," published as a separate chapter of the volume "Mineral Resources of the United States in 1909."

SYNTHETIC CAOUTCHOUC.

By FRANK E. BARROWS, Assistant Examiner, United States Patent Office.

Under this title a most comprehensive review of the literature on the subject of the "Synthetic Production and Constitution of Rubber" has been published in the May number of the *Armour Engineer*.

Besides quoting most completely from all publications on this subject and giving especially valuable extracts from the recent articles of the Russian investigator, Lebedeff, the author propounds a most interesting and plausible new theory on the polymerization of diolefins and the formation of rubber. The study of the article is highly recommended to everybody interested in the subject.

GEM IMPORTS.

The imports of precious stones and pearls for May as reported by Francis W. Bird, appraiser of the port, shows that receipts of this character are increasing in value. The value of imports of gems, including pearls, during May was \$2,663,829, compared with \$2,717,082 in May one year ago, and \$2,689,213 two years ago. The invoices and appraisement orders received during May are stated to be 34,162 while in the same month one year ago they were about 1,000 less.

AUTOMATIC GLASS BLOWERS.

In its May issue *The American Flint* states that the Owens Bottle Machine Co. has perfected a machine that produces 10 one-gallon packers per minute, and a machine that makes 47 prescription bottles per minute. It is further stated that the prescription machine is capable of making from 2- to 10-ounce bottles.

GENERAL NOTES.

The United States Civil Service Commission announces the postponement to July 5, 1911, of the examination announced to be held on May 24, 1911, to secure eligibles from which to make certification to fill three or more vacancies in the position of assistant in the paper and textile laboratories of the Bureau of Standards, at salaries ranging from \$900 to \$1,600 per annum.

As an insufficient number of applications were re-

ceived for the examination for this position announced to be held on May 24th, qualified persons are urged to enter this examination.

James Smith, chairman of the manufacturing committee of the Standard Oil Co., died on May 15th in New York City, of apoplexy at the age of 53 years. He had been with the Standard Oil Co. for 38 years. It is said that Mr. Smith was the first man to succeed in refining Texas oil.

The Pelham Phosphate Co., of Pelham, Ga., is erecting a plant for manufacturing acid phosphate and sulphuric acid. The plant will have an annual capacity of 15,000 tons of acid phosphate.

Dr. Edward B. Voorhees, director of the New Jersey Agricultural Experiment Station and Professor of Agriculture at Rutgers College, died on June 6th, of paralysis.

A fire resulting from the explosion of 200 gallons of paint stored in her hold burned the lake passenger steamship *Northwest* at Buffalo, the damage totaling \$500,000.

An anonymous colliery owner through Winston Churchill, British home secretary, offered a prize of \$5,000 for an efficient electric safety lamp.

CONSULAR AND TRADE NOTES.

TEXTILE YARNS AND FABRICS FROM PAPER.

Consul Augustus E. Ingram refers to an interesting paper read at the recent meeting at Manchester of the Textile Institute, by Carl Pontus Hellburg, of Halmsted, Sweden, on *Pine Fiber: A New Fiber for Textile Manufacturing*. Mr. Hellburg, who has studied paper spinning for 10 years, traces the history of this art from the hand-spun paper twines and yarns used years ago in China and Japan to the attempts in the United States some 20 years ago to spin paper yarns for textile purposes.

The manufacture of yarns spun from wood pulp or half-made paper was attempted for many years in Germany, and at Waldhof, near Mannheim, the so-called "Licella yarn" was produced, but the yarn department of these works was closed in 1907-8 in consequence of unsuitable machinery, the high cost of production, and the unsatisfactory strength of the yarn.

A superior pulp yarn called "silvalin" was first made at the Elberfeld paper mill, but in 1909 the works were transferred to Hammern, Rheinland, Germany. The method of production employed, according to Mr. Hellburg, is unsuitable for building up a large industry, there being too much waste and too great a difficulty in keeping the rolls sufficiently moist for a few hours until the spinning process takes place. Therefore, Mr. Hellburg says:

"In order to obtain an absolutely first-class yarn from pine fiber, finished paper made from the very best sulphite or sulphate pulp must be used, this pulp to be made from the slowly growing white pine which is found in Russia, Finland, Sweden, Norway, Canada, and the United States. The spinning of yarn from finished paper gives that yarn a suitable strength. It has also been proved by the trials I have made that Swedish Kraft paper gives a yarn 20-25 per cent. stronger than other kinds of paper."

Putting aside the advantage of obtaining a stronger yarn by using finished paper instead of pulp, there is no saving in producing yarn from the pulp direct, as the pulp, or half-made paper as it should be called, in order to be spun has to be subjected to the same treatment as in making paper, with the exception of the finishing.

Paper yarn for textile purposes, called xylolin, is manufactured in Saxony and Austria, and is used for backing carpets

and for making carpets composed exclusively of paper yarn. [Samples of xylolin are on file at the Bureau of Manufactures.] The cost of production by the Claviez method is rather high, partly because the spinning mills do not make their own raw material—the paper itself; and partly because the machinery employed is not altogether satisfactory. Mr. Hellburg has consequently invented and patented a combined cutting, dividing, and rolling-to-bobbin machine. Mr. Jagenberg, of Dusseldorf, has constructed a ring-spinning machine for paper which works satisfactorily and requires only one employee at each side of the 100-spindle machine as against two for the Claviez machine of 120 spindles. The new method consists of 9 operations as against 102 in the old method.

The appearance and strength of the yarn will depend on the quality of the paper. From Swedish Kraft a very strong yarn is obtained. Pure sulphite paper which is not mixed with mechanical pulp also produces a serviceable yarn, which is good for many purposes. For specially fine yarn tissue paper is the best. At present there is no paper specially made for spinning purposes, and all Mr. Hellburg's trials have been made with common wrapping paper, the results obtained being exceedingly good. So far, coarse counts only have been produced.

Paper intended for spinning should be about 19 inches wide and in rolls; these are placed in the cutting machines, which cut the entire width in one operation in strips of one-sixth to one-half an inch or any required width. The strips thus obtained are simultaneously carried over to the dividing and rolling-to-bobbin machine, and are cut at a speed of about 44 yards per minute. They are separated and rolled on the bobbins in lengths of about 3,000-5,000 yards on each bobbin. These bobbins are then removed to the spinning machines, with one bobbin for each spindle, and the paper strip from each bobbin is carried to a dampening roller, and directly after leaving this roller is spun into yarn on a ring spindle, either upon a wooden bobbin or a conically shaped paper tube. The spinning production averages about 356 pounds per 100 spindles in 10 hours.

With regard to the uses of this paper yarn, packing twine and cord have been made; and samples of these and several other manufactures are forwarded [and will be loaned to interested firms by the Bureau of Manufactures.] Spindle bandings have also been cheaply made and have the additional advantage of

being easily washed without fraying. The cotton of which these hands are usually made could be saved for other purposes.

Carpets of all-paper yarn are already in great demand. In carpet backs the paper yarn is said to be superior to jute yarn. It is also useful for floorcloth for linoleum and in such linen fabrics as paddings, waterproof canvas, scenery cloth, etc., the paper yarn can be used as weft. There are many other fabrics to be made of a union of paper yarn and cotton such as upholstery, cloth, mattress cloth, etc. Trimmings for curtains and furniture have also been made, composed of a paper yarn overspun with silk. Samples of white paper yarn dyed in the hank are also forwarded; to insure thorough penetration of the dye, the dyeing should be effected in the pulp.

As a substitute for jute it may be very welcome for bags, sacks, and packing cloth. For wool packs a cloth of all-paper yarn would be very suitable because of its clean surface; the objectionable presence of vegetable fiber in wool might thus be lessened.

It is claimed that this paper yarn is not damaged by hot or cold water. Paper yarn tarpaulin was alternately boiled, air-dried, immersed in cold water, and ironed without suffering damage. [The full text of the inventor's address on "Pine Fiber for Textile Manufacture" may be obtained from the Bureau of Manufactures.]

NEW METHOD OF WOOD PRESERVATION.

A chemical process for the preservation of wood is described in a report sent to the Bureau of Manufactures by Consul-General William A. Prickett. A limited company in New Zealand is now engaged in treating chemically lumber of ordinary quality for railroad ties, fence posts, etc., and the claim is made that the material so treated will last as long as the best wood the forests can produce.

The preserving process is said to be simple and inexpensive, and consists essentially in boiling the wood in a saccharine solution to which certain other substances are added according to the special purpose for which the lumber is required. The lumber is not subject to any external pressure or vacuum at any stage of the process. The wood as it is received is immersed in a cold solution in large open tanks. This solution is gradually raised to the boiling point and is maintained at this temperature for a certain time, depending on the size and density of the wood. After cooling, the wood is removed and placed in a drying kiln, the temperature of which is slowly raised. When sufficient desiccation has taken place the kiln is gradually cooled down. The time occupied by the whole treatment generally takes but a few days, though in special cases and for large-sized timber it may be extended for several weeks. The action which takes place is described as follows:

As a saccharine solution boils at a slightly higher temperature than water, the moisture in the wood is converted into vapor and escapes along with the air. During the boiling the albuminous matter in the wood is coagulated and rendered inert. In some measure this coagulation accounts for the strength of the wood being increased by this process. While cooling, the solution is rapidly absorbed by the wood and penetrates every part of it.

The company is executing an order for 180,000 sleepers for the Government Railway Department, and the works were lately inspected by the Prime Minister. The company is also treating large quantities of wood for use in railway cars and carriages.

Among the advantages claimed for this process is the statement that the timber can be treated as soon as it is brought in from the woods and then immediately used for the purposes required, whereas in the ordinary way the timber must be allowed to season before being worked up. It is claimed, also, that there is no waste in lumber which has been treated, as the process stops all warpage and splitting, as well as rendering it absolutely immune from dry rot and borer insects.

CANADA'S ASBESTOS SUPPLY.

According to an official report, Canada produces 82 per cent. of the world's supply of asbestos. The companies operating asbestos quarries and factories in Canada are capitalized at \$24,290,000. In 1880 only 380 tons of asbestos were produced in the Dominion, valued at \$24,700; in 1909 the output was 63,300 tons, valued at \$2,300,000. In 1909 2,000 men were employed in the asbestos industry, and received wages amounting to \$1,350,000. In the Black Lake quarries, in the Province of Quebec, there are 45,000,000 tons of asbestos rock in sight.

The asbestos slate or shingle industry is being developed by the plants in Canada, and predictions are made that in a short time 75 per cent. of all the asbestos produced in the Canadian quarries will be used for asbestos shingles. The asbestos-slate business is only five years old, but during that time the demand for this article has increased enormously, and large factories are being established to supply the demand for this new roofing material.

NATURAL GAS DISCOVERIES IN HUNGARY.

The Hungarian Government has decided to monopolize the tremendous natural gas source recently discovered at Kissarmas, in Transylvania, of which the daily yield amounts to 26,000,000 cubic feet. The gas comes out of the ground at a pressure of over 30 atmospheres, and the noise it makes is heard many miles away. The prices for land in the neighborhood have already increased tenfold, and Kissarmas, from being only a little hamlet lost in the mountains, promises to become a very important industrial center.

The Government engineers estimate that the yield will be sufficient to illuminate all the towns and villages in Transylvania, and also to bring over by pipes large quantities of gas to Budapest. Other borings for gas have already been commenced at Dieso-Szent-Marton, Ura Maros-Szent-Gyorgy, Sachshish-Regen, and Szent-Benedek.

The annual report of an artificial-silk factory near Frankfort shows a clear loss of \$346,052 for 1901. This same company in former years paid as high as 35 per cent. Shares, which at one time brought as high as \$133 on the local stock market, have been as low as \$23 and are now selling at \$30. The price of artificial silk has dropped 60 per cent. in the last few years, being now \$1.20 per pound.

BOOK REVIEWS.

Nitrocellulose Industry. By EDWARD C. WORDEN. Vol. II. Octavo, xxviii, 672 pp., 176 illustrations. D. Van Nostrand Co., New York, 1911. Price, \$5.

The review of the first volume of the "Nitrocellu-

lose Industry" appeared in the June number of THIS JOURNAL. The general criticism of the work there given also applies, for the most part, to the second volume, which includes the following additional sub-

jects: celluloid and the pyroxylin plastics, including a historical account; the compounding, rolling, pressing and sheeting of celluloid; the process of making the various kinds of mottled stock; the fashioning of celluloid into the many articles used in the arts; celluloid substitutes; the analysis of celluloid; and a list of English and United States patents relating to the pyroxylin plastics: the use of cellulose nitrates in microscopy, pharmacy, medicine, and photography; the manufacture of smokeless powder and high explosives, with description of the various forms prepared for the trade and the more important stability tests; the manufacture and uses of cellulose acetate and viscose; United States regulations for the use of denatured alcohol; appendix including patent, name and subject index.

In treating the above subjects the author has laid special stress on the pyroxylin plastics, the chapter on this subject being really a book in itself. In it are included descriptions of nearly all the important processes used in the manufacture of celluloid, gathered from a careful search of the patents and literature and from personal contact during many years with those engaged in the industry. The account differs favorably from that appearing in a recent work on celluloid by giving the preponderance of space and emphasis to the preparation of celluloid from the raw materials instead of to the fashioning of the finished product. The author has included in this account a great many obsolete or impracticable processes, intentionally for the sake of completeness, as explained in the preface, but in many cases without indicating either by order of presentation or otherwise which are the essential and which the non-essential facts. For example, there are a number of descriptions of processes proposed or patented by J. Edson, a man who did not make a success of the celluloid business and went into a different line of work many years before his death.

The chapter on the use of cellulose nitrates in photographic films contains a great deal of interesting information but the author often wanders far from his subject and writes much that might better be included in a treatise on photography.

"Guncotton, Smokeless Powder and Explosive Cellulose Nitrates" opens with the statement that the subject matter is incomplete as compared with the other sections of the work, the object being to record the more important facts. It is unfortunate that the other sections were not written with this same object for here one may readily get at the essential operations, the descriptions of which are accompanied by reproductions of photographs taken from a large plant. More specific descriptions are given in notes in finer print and the general arrangement of the chapter is excellent. The reader is enabled to learn the steps necessary to produce the finished explosive and to obtain a good idea of the different types now in use. This has been accomplished without sacrificing the author's object stated in the preface, of not having the text leave off at just that point where specific information is most desired.

Cellulose acetates are described from a chemical as well as technical point of view and a translation is given of a notable contribution to the subject by C. G. S. Schwalbe. Here, as in the rest of the work, the information has been brought up to date in a manner unusual in a book of this kind.

The above subject as well as the chapters on viscose and denatured alcohol which follow are out of place in a book on the "Nitrocellulose Industry," but their presence may be pardoned on the ground that the work is probably destined to reach many small libraries where it will form a comprehensive and valuable addition.

C. M. JOYCE.

The Iron Ores of Lake Superior. Containing Some Facts of Interest Relating to Mining and Shipping of the Ore and Location of Principal Mines, with Original Maps of the Ranges. By CROWELL AND MURRAY, Chemists and Metallurgists Cleveland, Ohio. The Penton Publishing Co., Cleveland.

The book opens with a short history of the Lake Superior district, stating that iron ore was first discovered in Michigan in 1844. First iron made in an old forge on Carp River 5 miles east of Negaunee, February 10, 1848. First shipment of ore from Lake Superior region was made July 7, 1852, six barrels being the consignment. First ship canal around the rapids at Sault Ste. Marie was completed in 1855—regular shipments by boat in 1856.

The geology of the region is given, briefly outlining the important features in the various ore-bearing districts. Eight pages are devoted to mining methods, transportation and classification of ores.

The method of sampling ores adopted by the Independent Chemists of Cleveland is given in full, followed by methods of analysis that are in general use.

One hundred and forty pages are devoted to descriptions of 365 mines, this including nearly all of the mines on the different ranges. This description gives location, date opening of mine, nature of the ore, system of mining, greatest vertical depth of mine, road over which ore is shipped from mine, sales agent, yearly shipments, total tons shipped, and average analysis dried and natural of ore shipped for the season of 1910.

As stated in the preface, much of the information contained in the book has appeared in the various trade journals, geological reports and scientific society transactions.

The authors have, however, compiled these scattered facts and presented this information in a very acceptable and concrete form. To this they have added, as stated above, a late description of most of the mines on the different ranges and have worked out maps showing their exact location.

To any one desiring information relative to the iron ores of Lake Superior, I would recommend this book.

WILLIAM BRADY.

"The Chemistry of Coal Tar Dyes." By IRVING W. FAY. D. Van Nostrand Co., New York. 1911. 365 pages; \$4.00 net.

This volume is an attempt to develop in a somewhat systematic manner the chemistry of the more important coal tar dyes. The author has succeeded in

making a book which will, without doubt, prove interesting to the student of dyestuffs, though it will require considerable previous knowledge of organic chemistry to appreciate the large amount of theoretical chemistry contained in this book. In fact, the author has concerned himself principally with the theory of the subject, chiefly with the idea, it would seem, of describing the structural formulas of the various dyestuffs. Though the book will be of value to the student as an amplified chapter in general organic chemistry, it cannot be of much use to the practical dyer, who would only be utterly dumbfounded by the array of complicated structural formulas, presented and who would look in vain for any proper technical matter relating to the properties and methods of application of the various dyestuffs described.

Unfortunately, the value of this book as a contribution to scientific literature is greatly marred by various crudities of style and diction. As a whole, the material appears to be rather slovenly and uncritically thrown together. The sentence, for instance, on page 5, commencing "If coal be heated equally hot," reminds one unfortunately of Freshman attempts in prose composition. Under the description of nitrobenzene we find the following: "In commerce it is known as 'nitrobenzole for blue' or 'nitro benzole for red'; the first is principally used in the manufacture of aniline for blue; the latter is used for preparing aniline for reagents." There is nothing to indicate to the reader the difference which must exist in these two varieties of nitrobenzene. "Piesic acid is the final oxidation product of many aromatic substances" is an inaccurate statement. In speaking of naphthol yellow the author writes: "On account of the sulpho group, which this possesses over Martins yellow, it is a more valuable dye. It is more soluble and acids cause no precipitate in its yellow solution." This would lead us to infer that acids would cause a precipitate if its solution were some other color. These examples of bad styles occur scattered generally throughout the entire book, and detract a great deal from the reader's appreciation of its otherwise many good qualities. In this connection we cannot help quoting one of the early sentences in the book, which surely must be a literal translation of a German original, for we cannot conceive of an American mind of itself ascending to such heights of literary

structure: "From the early manufacture, of a nature so crude that during suits, in Paris in the early days, of one manufacture against another for infringements of patents neither counsel nor experts could either dispute or establish the identity of products made by different oxidizing agents upon the same raw materials, to the present day, when research is often able to reveal the actual structure and how the complex dye molecule is built up, is a long history of processes which have been improved by a most persistent and thorough study, both theoretical and practical, by the celebrated investigators of the scientific world." Truly wonderful!

This book also exhibits careless inconsistencies in spelling the same word, such as "alizerine and alizarin," "chromophor and chromophore," "amido and amino." The author probably means "generic" when he speaks of "the genetic relation." In writing of the substantive cotton dyes on page 142, he calls them "dye salts" when he should have said "salt dyes." In the chapter on triphenylmethane dyes, the page heading "triphenylmethane" is misspelled three times in the space of a few pages, and there are numerous other evidences of careless proof-reading. In the section on "ingrain colors" (which by the way is an obsolete term), the author seems unaware of the existence of primuline, which is the most widely known and extensively used of this group of dyes. Also, the new and very important, as well as very highly interesting, group of vat dyes is not mentioned, with the exception of credigo and a few indigo products. The author is apparently ignorant of the indanthrene dyes, and the other groups of dyes of this same nature. The chapter on sulphur dyes is also very out-of-date, and does not at all represent the condition of the science at the present time, and most of the products treated are now unimportant or totally obsolete. In the chapter on mordants, the author unfortunately has gotten hold of some very archaic matter. The description of mordanting cotton with alum (on page 401) reads almost like an extract from a medieval book on dyeing, especially the last sentence: "The cotton is then washed without losing what it has gained by this treatment and the now mordanted fiber will absorb the various shades of color and hold them securely, beyond the power of water to remove." J. MERRITT MATTHEWS.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

Quartz-glass: Its History, Manufacture and Uses. By P. GUENTHER. 8vo., 52 pp. Berlin. (German.)

The Chemistry of Honey. By O. HAENLE. 4th Edition. I. 8vo., 80 pp. \$1.25. Strassburg. (German.)

Directory of American Gas Companies—1911. By E. C. BROWN. 8vo., 641 pp. \$5. Press of Progressive Age, New York.

Engineering Chemistry. By THOMAS B. STILLMAN. 4th Edition. 8vo., 744 pp. \$5. The Chemical Publishing Co., Easton.

Chemist's Pocket Manual. By RICHARD K. MEADE. 2nd

Edition. 8vo., 544 pp. \$3. The Chemical Publishing Co., Easton.

Directory of the Entire Glass Industry of Europe. Vol. I. Germany, 1911. No author. Sm. 8vo. 295 pp. \$1.25. Schulze & Co., Leipzig. (German.)

Transformer: A Treatise on the Theory, Construction, Design, etc. By H. BOHLE AND D. ROBERTSON. 8vo., 370 pp. \$5.25. C. Griffin, London.

Modern Explosives. By P. F. CHALON. 3rd Edition. 8vo., \$5. Ch. Béranger, Paris.

- Short Textbook of Radioactivity. By P. GRUENER. 2nd Edition. L. 8vo., 119 pp. 75c. A. Franke, Bern. (German)
- General Agricultural Chemistry. By E. B. HART AND W. E. TOTTINGHAM. 120, 334 pp. \$1.50. Privately printed (E. B. HART), Madison, Wisc.
- Transportation of Gases, Liquids and Solids. By OSKAR NAGEL. 8vo., 200 pp. \$2.50. Vacher & Sons, London.
- Physico Chemical Tables. Vol. II. Physical and Analytical Chemistry. By CASTELL-EVANS. 1220 pp. \$12. J. B. Lippincott Co.
- Dictionary of Electrical Engineering. By HOBART. 2 Vols. \$10. J. B. Lippincott Co.
- Methods of Modern Sewage Purification. By G. BERTRAM KERSHAW. 340 pp. \$7.50. J. B. Lippincott Co.
- Alchemy: Ancient and Modern. By H. STANLEY REDGROVE. \$1.25. Wm. Rider & Son, London.
- Acetylene: Its Properties, Generation and Uses. By J. H. VOGEL. 8vo. \$4. O. Spamer, Leipzig. (German.)
- Chemical Technology of Paper. By G. DALÈN. 120 pp. \$1. J. A. Barth, Leipzig. (German.)
- Chemical Technology of Glass. By BERNHARD MUELLER. 103 pp. 50c. J. A. Barth, Leipzig. (German.)
- Chemical Technology of Leather. By JOHANNES PAESSLER. 18 pp. 50c. J. A. Barth, Leipzig. (German.)
- Chemical Technology of the Fats, Oils and Waxes. By C. STIEFEL. 146 pp. \$1.25. J. A. Barth, Leipzig. (German.)
- Rubber and Its Examination. By F. W. HINRICHSEN AND K. MEMMLER. 254 pp. \$2.25. S. Hirzel, Leipzig. (German.)
- Chemical-technical Lexicon. By JOSEPH BERSCH. 2nd Edition. \$4.50. A. Hartleben, Leipzig. (German.)
- Essential Oils: Semi-annual Report of Schimmel & Co., April 11. Schimmel & Co., Miltitz. (German and English.)
- The Fats. By J. B. LEATHES. 138 pp. \$1.20. Longmans, Green & Co., New York.
- The Rubber Country of the Amazon. By HENRY C. PEARSON. 8vo., 250 pp. \$3. India Rubber Publishing Co., New York.
- Elements of the Metallurgy of Iron. By T. GEELINKIRCHEN. Vol I., 8vo. \$2. J. Springer, Berlin. (German.)
- Gmelin and Kraut's Handbook of Inorganic Chemistry. 7th Edition. Zinc, Cadmium and Indium. By W. ROTH. Vol. IV, Part 1. L. 8vo., 1056 pp. \$11. Heidelberg. 1911. (German.)
- Gmelin and Kraut's Handbook of Inorganic Chemistry. 7th Edition. Phosphorus, Boron and Carbon. By GUTBIER. Vol. IV, part 3. L. 8vo., 907 pp. \$9. Heidelberg. 1911. (German.)
- Treatise on Inorganic Analysis. By A. CARNOT. Vol. III. 8vo. \$5.50. Paris. 1911. (French.)
- Yearbook of Organic Chemistry. By J. SCHMIDT. Vol. IV. for 1910. L. 8vo. \$4. Ferdinand Enke, Stuttgart. (German).
- Sulfur Tars: Their Production and Treatment. By W. SCHEITHAUER. 8vo. \$2.50. O. Spamer, Leipzig. (German.)
- Chemical Technical Methods of Analysis. By GEORG LUNGE AND ERNST BERL. 6th Edition. Vol. III. 8vo., 1044 pp. \$6. Julius Springer, Berlin. (German.)
- Electrically Controlled Constant Temperature Water Bath for the Immersion Refractometer. By H. C. GORE. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular No. 72.
- Enological Studies. By WM. B. ALWOOD. U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin, No. 140.

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

- Manufacture and Properties of Hydrated Lime. By RICHARD K. MEADE. *Engineering News*, May 11, 1911, pages 554-559.
- Analysis of Crude Glycerin. By W. GRUENEWALD. *Zeitschrift fuer angewandte Chemie*, xxiv, No. 19, pp. 865-870. (German.)
- Physical and Chemical Properties of Portland Cement. By W. C. REIBLING AND F. D. REYES. *Philippine Journal of Science*, A, Vol. V., No. 6, pp. 367-417.
- Natural Dyes and Coloring Matters of the Philippines. By B. T. BROOKS. *Philippine Journal of Science*, A, Vol. V., No. 6, pp. 439-452.
- Some Experiments Relating to Hops and Yeast. By HAROLD W. HARMON. *Journal of the Institute of Brewing*, Vol. XVII, No. 4, pp. 359-383.
- Raw and Pasteurized Milk and Milk Serums. By EDWARD GUDEMAN. *Illinois Medical Journal*, April, 1911.
- The Role of Slag in our Metallurgical Processes. By CARL DICHMANN. *Stahl und Eisen*, May 11, 1911, pp. 749-759. (German.)
- Significance of Lead Arsenate Composition. By W. H. VOLCK. *Science*, June 2, 1911, pp. 866-870.
- A Plea for the Use of References and Accuracy Therein. By F. ALEX. McDERMOTT. *Science*, June 2, 1911, pp. 852-853.
- Nature of the Combination between Fiber and Dye. By JEROME ALEXANDER. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 9, pp. 517-518.
- Viscosity of Nitrocellulose Solutions. By C. PIEST. *Zeitschrift fuer angewandte Chemie*, 1911, Heft 21, pp. 968-972. (German.)
- Asbestos as a Commercial Product. ANONYMOUS. *India Rubber World*, Vol. XLIV, No. 1, pp. 235-236.

RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

987,850. Process of Treating Ores.

This is a process for treating metalliferous ores, particularly those bearing the more valuable metals, such as gold, silver copper, etc., and the invention resides in taking uncrushed ores as they come from the mines or after they have passed through the primary breakers and alternately lifting and dropping the same onto a hard surface or surfaces within a container whereby to pulverize the ores, and while dropping subjecting such ores to a high temperature by dry heat to drive off the water of crystallization and volatile products in the ore and render the ore mass spongy and cause the same to decrepitate, thereby assisting

in breaking and crushing the ore on impacting with the hard breaker body so as to pulverize the ore.

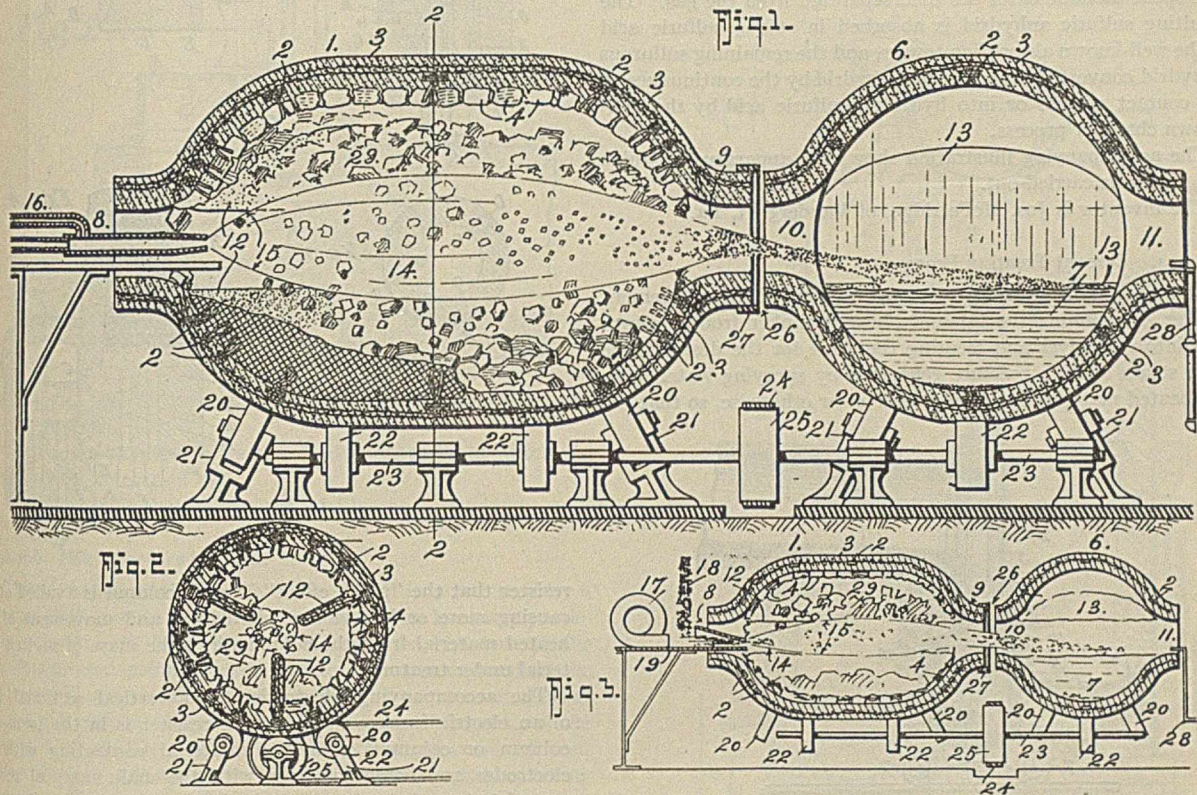
In the use of the apparatus shown in the accompanying illustration, the ore 29 to be treated is placed in the container 1 and the fuel for heating is also introduced when the oil burner 16 is used to produce the heat blast from inlet to outlet of the container 1. Having introduced the ore in large chunks as it comes from the mine (or after it has passed through the first breakers) into the container 1 and having introduced the solvent into the container 6 (the solvent being a cyanid or other solution when gold and silver ores are undergoing treatment) a hot blast is

produced by igniting the burner 16 in any desired manner, and the containers are set in motion. The ore 29 will be carried up by the partitions 12 and 13 and dropped through the blast or flame 15 where they will come into direct contact with the hot blast and have their water of crystallization and volatile products driven off. Any sulphur in the ore will be removed in this manner. The ore having dropped through the hot blast 15 impacts the crusher surface 4 of the container at the bottom and inasmuch as the structure of the ore in being heated is weakened and made porous, the impact will break and crush the ore, which breaking and crushing is further assisted by the rolling and tumbling of the softer particles in connection with the

practically so, so as to avoid the boiling of the solvent but still allow sufficient heat to assist the chemical reaction.

As soon as a sufficient quantity of ore is deposited in the solution 7 in the container 6, said container is rolled away and another container substituted. The dissolved ore and solvent from the container 6 which has been rolled away may be emptied after forced percolation by steam or vacuum, or both, and extracting the values thereby into any suitable reservoir where it may be further treated by the usual means to separate the dissolved values if any remain.

The inventor is Isaac A. Braddock, of Haddonfield, New Jersey, assignor of one-sixth to William C. Cood, of Baltimore



harder particles in the container 1 during its rotation. The temperature within the container 1 is usually carried up to about 500° F. so as to thoroughly dry the ore and drive off the volatile products.

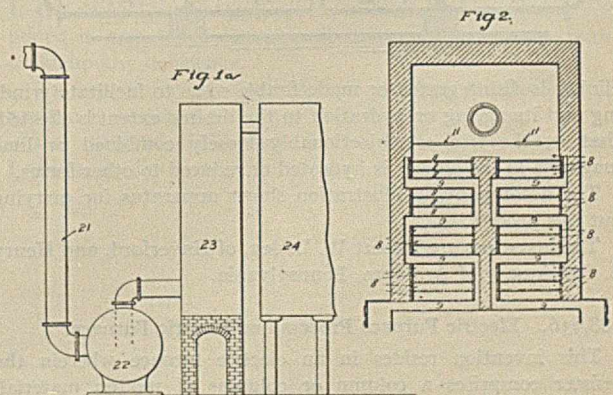
Attention is called to the fact that the removal of the volatile products in the ore while passing through the heat zone causes decrepitation to take place, and the ore becomes porous and spongy so when it contacts the bottom of the container it will be broken and crumbled, the breaking and crumbling action being also assisted by the rolling and tumbling of the ore within the retort during its movements, the heavier and lesser heated ores serving to assist in crushing the softer particles until the ore is reduced to a fine powder. The force of the heated blast serves to cause the crushed particles of the ore to gradually work toward the outlet 9 of the container and as soon as the ore rocks have been crushed fine enough the heated blast will carry the ore particles through the outlet 9 of the retort 1 into the second container 6 where the hot ore particles are deposited into the solvent 7. The container 6 being provided with partitions 13 will serve to agitate the solution within the container 6 and as the hot ore particles are directly deposited into said solution the temperature within the container 6 will be maintained at the desired degree (usually from 200° to 212° F.). The air opening between the containers 1 and 6 is so regulated that the temperature within the container 6 will be maintained constant or

Maryland, and one-sixth to Nicholas A. Kestler and one-sixth to David E. Anthony, of Washington, District of Columbia.

988,646. Process of Making Sulfuric Anhydrid.

This invention relates to a process of manufacturing sulfuric anhydrid from iron and copper pyrites, sulfid ores, and mattes resulting from the treatment of such ores.

In carrying out the process, sulfur-bearing ores or mattes, preferably fines, on account of their lower commercial value,



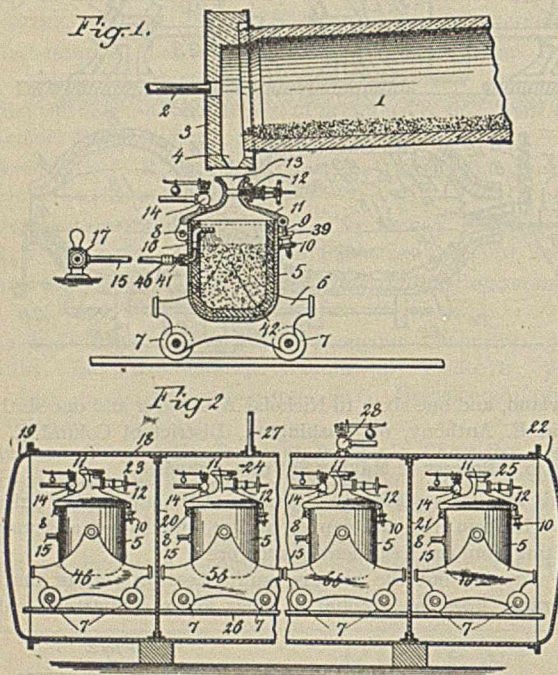
are ground to an impalpable powder. This is then fed into a furnace, kiln or shaft, heated to a temperature high enough to ignite the sulfur, preferably being fed by an air blast or drawn into the furnace by a fan or blower suction. The pulverulent ore is at once ignited, with formation of sulfurous anhydrid and metallic oxids. The finely divided metallic oxids are carried along in the furnace with the mixture of sulfurous anhydrid and air, and being in such a fine state of division, act at once as a catalyzer, converting 30-40 per cent. of the sulfurous anhydrid into sulfuric anhydrid, and at the same time the gases are purified by the removal of arsenic and the like by their intimate contact with the fine non-volatile oxids. The spent metallic oxids are then separated from the gas. The resulting sulfuric anhydrid is absorbed in strong sulfuric acid in the well-known absorption towers, and the remaining sulfurous anhydrid converted into sulfuric anhydrid by the continuance of the contact process or into hydrated sulfuric acid by the well-known chamber process.

The accompanying illustration shows the apparatus in which the process is carried out.

The inventor is Jos. McFetridge, of Vandergrift, Pa.

988,724. Cement Treating Process.

This invention is a process for treating Portland cement clinker, by running the intensely heated clinker from a rotary kiln into a receiver and treating the same for the desired time with steam at high pressure generated by spraying water upon the heated material in a closed receiver or otherwise, so that the



clinker is disintegrated or made friable so as to facilitate grinding and its ageing or hydration to the desired extent is effected, that is, the free or objectionably loosely combined or lime magnesia in the clinker is hydrated or reduced to other forms.

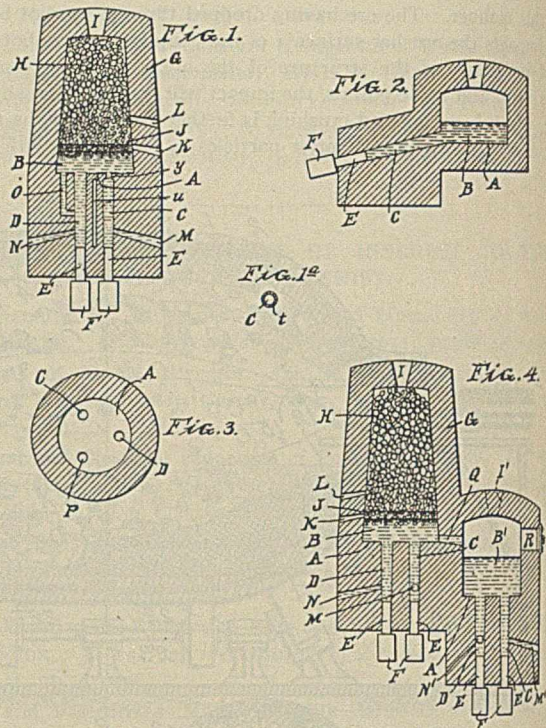
The accompanying illustration shows apparatus for carrying out this process.

The inventors are Robert W. Lesley, of Haverford, and Henry S. Spackman, of Ardmore, Pennsylvania.

988,936. Electric Furnace Process and Electric Furnace.

This invention resides in an electric furnace wherein the resistor comprises a column or columns of molten material, electrodes furnishing communication with the columns, the

heat in the column resistor being communicated to the main body or mass of molten or other material under treatment by conduction from such resistor and chiefly by convection and rapid circulation; and it is a further feature of the invention that the patentee so constructs and proportions the column



resistor that the "pinch effect" in such column is availed of for causing more or less violent circulation and movement of the heated material from the columns into the mass of molten material under treatment.

The accompanying illustration is a vertical sectional view of an electric furnace in which the resistor is in the form of a column or columns of molten material contacting with the electrodes and communicating with the main mass of molten material above it.

The inventor is Carl Hering, of Philadelphia, Pa.

988,963. Manufacture of Lead Oxid and White Lead.

In the manufacture of white lead from oxid by dissolving the latter in acetate of lead solution, nearly half the lead remains behind as sludge. This is owing to the oxid of lead having been fused in its manufacture, and no matter how finely it is ground afterward, this fused oxid is in large part insoluble in the acetate of lead solution.

It is the purpose of this invention to avoid the fusing of the oxid altogether by making it as a highly soluble massicot at a temperature a long way below the fusing point, and thus the difficulty hitherto experienced in working commercial litharge is avoided. Further, in the manufacture of red lead it is also very desirable to have the lead oxid in as fine a state of division as possible to avoid the fusing of the oxid, and to have every particle of the charge at the same degree of oxidation, and especially to avoid powdered lead in the charge, as the lead takes much longer to oxidize to red lead than the fused oxid, and the fused oxid much longer than the finely divided unfused oxid. It is thus impossible to bring all the lead oxid at the same time to the right color, and individual parts are too much oxidized, and others too little.

The process is defined in the patent as consisting in subjecting metallic lead to a blast of air and steam, discharging the mixed

dust and gases in an upward direction, and at the same time heating said dust and gases to a degree slightly below that

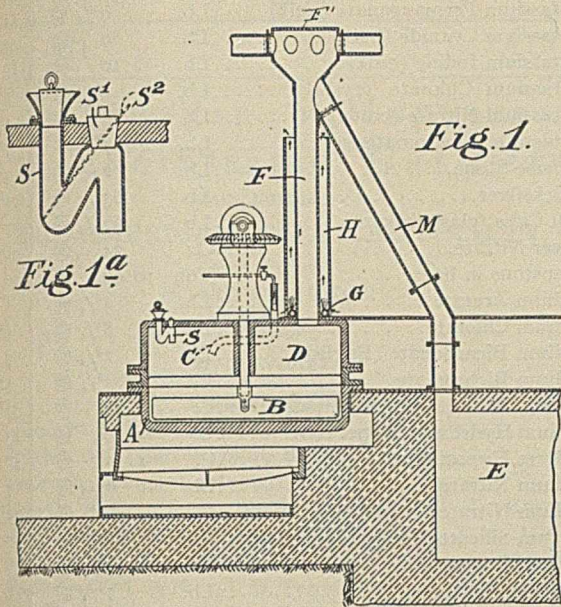


Fig. 1.

Fig. 1^a.

necessary to fuse the oxid until the entire lead contents are converted into oxid.

The accompanying illustration shows apparatus in which the process may be carried out.

The inventor is George Vincent, of Liverpool, England.

990,266. Manufacture of Steel.

This invention relates to the conversion of iron into steel by a process analogous to the Bessemer method and has more particular reference to improvements in what may be termed the continuous conversion process. In this last-named method the converter is of a stationary type, erected adjacent to or even as part of the cupola, whereby molten cast iron, the product of the cupola, is allowed to pass directly from the cupola hearth continuously into the converter through a conduit or connecting passage. The metal accumulates in the converter, to which blast, under suitable pressure is applied, causing the carbon, and other metalloids to be oxidized and the heated products of combustion to pass up into the cupola and assist in the reduction and melting of the metal. Thus the process of smelting and converting are carried on simultaneously, the bath of molten steel being constantly fuel enriched by passing over of highly carbonized iron from the cupola, and a sufficiently high temperature maintained to insure the combination of the oxygen in the blast with the carbon of the metal, the converter hearth being tapped intermittently for steel, as the molten metal accumulates and gets deprived of its carbon and other metalloids by the action of the air blast. Hitherto in this method of manufacturing steel, there has been excessive slagging, from the converter and the too free passage of molten metal intermingled with slag from the converter resulting in abnormal losses of metal that pass out with the slag while the

converter is in blast. Further, owing to the fact that an ordinary charge such as may be used for this process frequently consists of pig iron, steel scrap, and wrought iron, there is a lack of uniformity in the metal passing into the converter, and the steel is difficult to grade.

Now the object of the present invention is to obtain a purer and more uniform quality of steel. For this purpose there is formed a bath or well at the bottom of the cupola in which the molten metal accumulates and from which it overflows into the converter attached. This bath is supplied with twyers similar to those in the converter in order to thoroughly agitate and mix the molten metal, and remove by oxidation any excess of

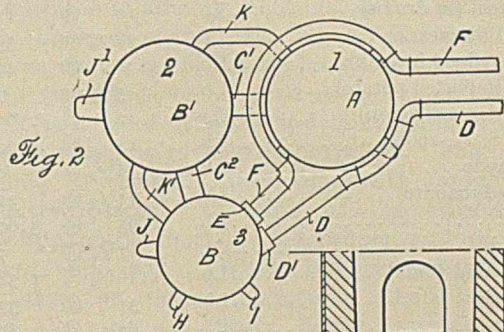


Fig. 2.

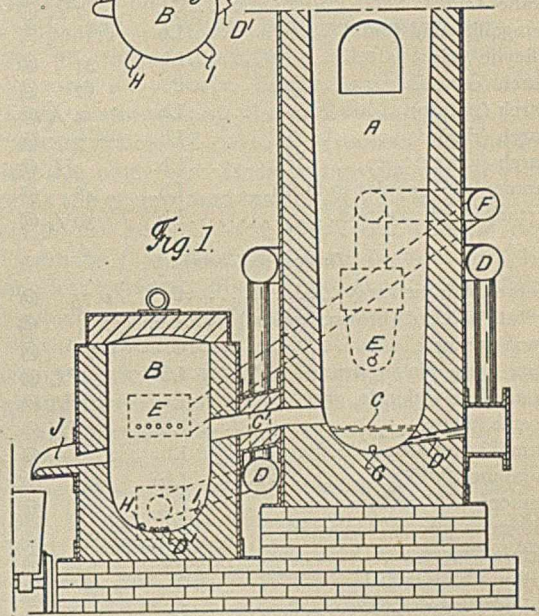


Fig. 1.

silicon, manganese or other impurities in the metal before it overflows into the said converter. The presence of the coke in the cupola bath prevents any appreciable reduction in the quantity of carbon in the metal, so that the metal overflowing into the converter does not contain more silicon and manganese than is required to be removed before the carbon is reduced to the desired percentage, but if found necessary carbon may be added in any convenient way to the converter or the bath to make up any deficiency.

The accompanying illustration shows apparatus in which the process is carried out.

The inventor is Thomas James Heskett, of Westminster, London, England.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JUNE.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Aetancilid.....Lb.	20 ¹ / ₂	@	23
Acetone (drums).....Lb.	13 ¹ / ₂	@	16 ² / ₃
Alcohol, grain (188 proof).....Gal.	2.50	@	2.54
Alcohol, wood (95 per cent.).....Gal.	50	@	52
Alcohol, denatured (180 proof).....Gal.	40	@	42
Amyl Acetate.....Gal.	2.40	@	2.50
Acetic Acid.....C.	1.58	@	1.73
Aniline Oil.....Lb.	11 ¹ / ₂	@	11 ³ / ₄
Benzoic Acid.....Oz.	11 ¹ / ₄	@	12
Carbon Tetrachloride (in drums).....Lb.	8	@	12
Carbon Bisulphide.....Lb.	5	@	7
Chloroform.....Lb.	27	@	35
Carbolic Acid (in drums).....Lb.	10	@	11
Citric Acid (domestic).....Lb.	38 ¹ / ₂	@	39
Camphor (refined in bulk).....Lb.	46 ¹ / ₂	@	47 ¹ / ₂
Dextrine (imported potato).....Lb.	5 ¹ / ₂	@	7
Dextrine (domestic corn).....C.	2.42	@	2.63
Ether (U. S. P., 1900).....Lb.	14	@	20
Formaldehyde.....Lb.	8 ¹ / ₂	@	9 ¹ / ₂
Glycerine (dynamite).....Lb.	21 ¹ / ₂	@	22 ¹ / ₂
Iodoform.....Lb.	2.95	@	3.00
Oxalic Acid.....C.	7 ¹ / ₈	@	7 ³ / ₄
Pyrogallic Acid (bulk).....Lb.	1.16 ² / ₃	@	1.38 ¹ / ₂
Salicylic Acid.....Lb.	31	@	33
Starch (corn).....C.	1.67	@	1.83
Starch (potato).....Lb.	4 ¹ / ₄	@	4 ⁵ / ₈
Starch (rice).....Lb.	7	@	8
Starch (wheat).....Lb.	4 ¹ / ₈	@	5 ³ / ₄
Tannic Acid (regular in bulk).....Lb.	48	@	50
Tartaric Acid, crystals.....Lb.	30 ¹ / ₄	@	30 ³ / ₄

Inorganic Chemicals.

Acetate of Lime (gray).....C.	1.75	@	1.80
Acetate of Lead (brown, broken).....Lb.	7 ³ / ₄	@	8
Alum (lump).....C.	1.75	@	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 ³ / ₄	@	3
Ammonium Chloride, gray.....Lb.	5 ³ / ₄	@	6
Arsenic, white.....Lb.	1 ³ / ₄	@	2 ³ / ₄
Ammonium Carbonate, domestic.....Lb.	8	@	8 ³ / ₈
Aluminum Sulphate.....Lb.	90	@	1 ³ / ₄
Ammonium Vanadate.....Oz.	41	@	50
Brimstone (crude, domestic).....Ton	22.00	@	22.50
Barium Chlorate.....Lb.	15	@	17
Barium Chloride.....C.	1.90	@	2 ³ / ₄
Barium Nitrate.....Lb.	5 ¹ / ₂	@	6 ¹ / ₂
Borax, crystals in bags.....Lb.	3 ¹ / ₂	@	4
Boric Acid, crystals.....Lb.	7	@	7 ¹ / ₂
Bromine, bulk.....Lb.	25	@	30
Bleaching Powder (35 per cent.).....C.	1.17 ¹ / ₂	@	1.25
Barytes (prime white, foreign).....Ton	18.50	@	22.50
Blue Vitriol.....Lb.	4 ¹ / ₂	@	4 ³ / ₄
Calcium Chloride.....C.	65	@	90
Calomel, American.....Lb.	90	@	92
Chalk (light precipitated).....Lb.	4 ¹ / ₂	@	6
Cobalt Oxide.....Lb.	80	@	1.00
China Clay (imported).....Ton	11.50	@	18.00
Feldspar.....Ton	8.00	@	12.00
Fuller's Earth, powdered.....C.	80	@	85
Green Vitriol (in bags).....C.	60	@	85
Hydrochloric Acid (18°).....C.	1.15	@	1.75
Hydrochloric Acid (22°).....C.	1.45	@	1.75
Iodine (resublimed).....Lb.	2.60	@	2.65
Lead Nitrate.....Lb.	8	@	8 ¹ / ₂
Lithium Carbonate.....Lb.	57	@	60
Magnesite (raw).....Ton	10.00	@	11.00
Mercuric Chloride.....Lb.	81	@	84
Nitric Acid, 36°.....Lb.	3 ⁷ / ₈	@	4 ¹ / ₄
Nitric Acid, 42°.....Lb.	4 ⁷ / ₈	@	5 ¹ / ₂
Phosphorus.....Lb.	45	@	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21	@	25

Plaster of Paris.....C.	1.50	@	1.70
Potassium Bromide.....Lb.	31	@	34
Potassium Permanganate (bulk).....Lb.	9 ³ / ₈	@	11
Potassium Cyanide (bulk).....Lb.	20	@	24
Potassium Iodide (bulk).....Lb.	2.10	@	2.15
Potassium Chlorate, crystals.....Lb.	8 ¹ / ₄	@	9 ¹ / ₂
Potassium Nitrate (crude).....Lb.	4 ³ / ₄	@	5
Potassium Bichromate, 50°.....Lb.	7 ³ / ₈	@	7 ¹ / ₄
Pumice Stone.....Lb.	2	@	4
Quicksilver.....Lb.	63 ¹ / ₃	@	65 ¹ / ₃
Salt Cake (glass-makers).....Lb.	62 ¹ / ₂	@	77 ¹ / ₂
Silver Nitrate.....Oz.	34	@	36
Soapstone in bags.....Ton	10.00	@	12.00
Sodium Acetate.....Lb.	4 ¹ / ₄	@	5
Sodium Chlorate.....Lb.	8 ¹ / ₄	@	9 ¹ / ₄
Sodium Bicarbonate (English).....Lb.	2 ³ / ₄	@	3
Sodium Bichromate.....Lb.	5 ⁵ / ₈	@	5 ⁵ / ₄
Sodium Bisulfite (not incl. pkg.).....C.	75	@	1.37 ¹ / ₄
Sodium Hydroxide, 60 per cent.....C.	1.80	@	1.85
Sodium Hyposulfite.....C.	1.30	@	1.50
Sodium Nitrate.....Lb.	6 ¹ / ₈	@	7
Sodium Nitrate, 95 per cent., spot... C.	—	@	2.12 ¹ / ₂
Sodium Silicate (liquid).....C.	65	@	1.50
Sodium Stannate.....Lb.	9 ³ / ₄	@	10
Strontium Nitrate.....Lb.	7 ¹ / ₄	@	8
Sulphur, Roll.....C.	1.85	@	2.15
Sulphur, Flowers.....C.	2.20	@	2.60
Sulphuric Acid, 60° B.....C.	86 ² / ₃	@	1.00
Talc (American).....Ton	15.00	@	25.00
Terra Alba (American), No. 1.....C.	75	@	80
Tin Bichloride (50°).....Lb.	12 ¹ / ₂	@	12 ² / ₃
Tin Oxide.....Lb.	49 ¹ / ₃	@	51 ¹ / ₂
Tin Chloride (36°).....Lb.	11	@	11 ¹ / ₂
Zinc Chloride (granulated).....Lb.	4 ¹ / ₂	@	4 ¹ / ₂
Zinc Sulphate.....Lb.	2 ¹ / ₄	@	2 ¹ / ₂

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40	@	45
Black Mineral Oil, 29 Gravity.....Gal.	12	@	12 ¹ / ₂
Castor Oil (No. 3).....Lb.	10	@	11
Ceresin (yellow).....Lb.	9	@	20
Corn Oil.....C.	5.93 ¹ / ₃	@	5.98 ¹ / ₃
Cottonseed Oil (crude, f. o. b. mill).....Gal.	40 ⁵ / ₆	@	41 ¹ / ₂
Cylinder Oil (light, filtered).....Gal.	19 ¹ / ₂	@	20
Japan Wax.....Lb.	9	@	9 ¹ / ₄
Lard Oil (prime winter).....Gal.	78 ¹ / ₃	@	85
Linseed Oil (raw, city).....Gal.	88 ¹ / ₃	@	89 ¹ / ₃
Linseed Oil (double-boiled).....Gal.	90	@	91 ¹ / ₂
Paraffine Oil (high viscosity).....Gal.	23 ¹ / ₂	@	24
Paraffine (crude 120 @ 122 m. p.).....Lb.	3	@	3 ¹ / ₄
Paraffine (refined, domestic) 120 @			
122 m. p.....Lb.	4 ¹ / ₂	@	4 ¹ / ₂
Rosin Oil (first run).....Gal.	—	@	37
Spindle Oil, No. 1.....Gal.	14	@	14 ¹ / ₂
Stearic Acid (double-pressed).....Lb.	9 ¹ / ₂	@	9 ¹ / ₄
Sperm Oil (bleached winter) 38°.....Gal.	82	@	85
Tallow (acidless).....Gal.	64	@	66
Tar Oil (distilled).....Gal.	30	@	31

Metals.

Aluminum [No. 1 ingots].....Lb.	19 ³ / ₄	@	20 ¹ / ₄
Antimony.....Lb.	—	@	9
Bismuth.....Lb.	—	@	1.80
Copper (electrolytic).....Lb.	—	@	12 ¹ / ₂
Copper (lake).....Lb.	12 ¹ / ₂	@	13
Lead.....Lb.	4.40	@	4.42 ¹ / ₂
Mercury.....Lb.	61.3	@	61.5
Nickel.....Lb.	40	@	50
Platinum (refined).....Oz.	42.50	@	43.00
Silver.....Oz.	—	@	53
Tin.....Lb.	—	@	45 ¹ / ₃
Zinc.....Lb.	5.45	@	5.50