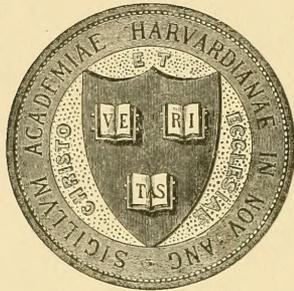


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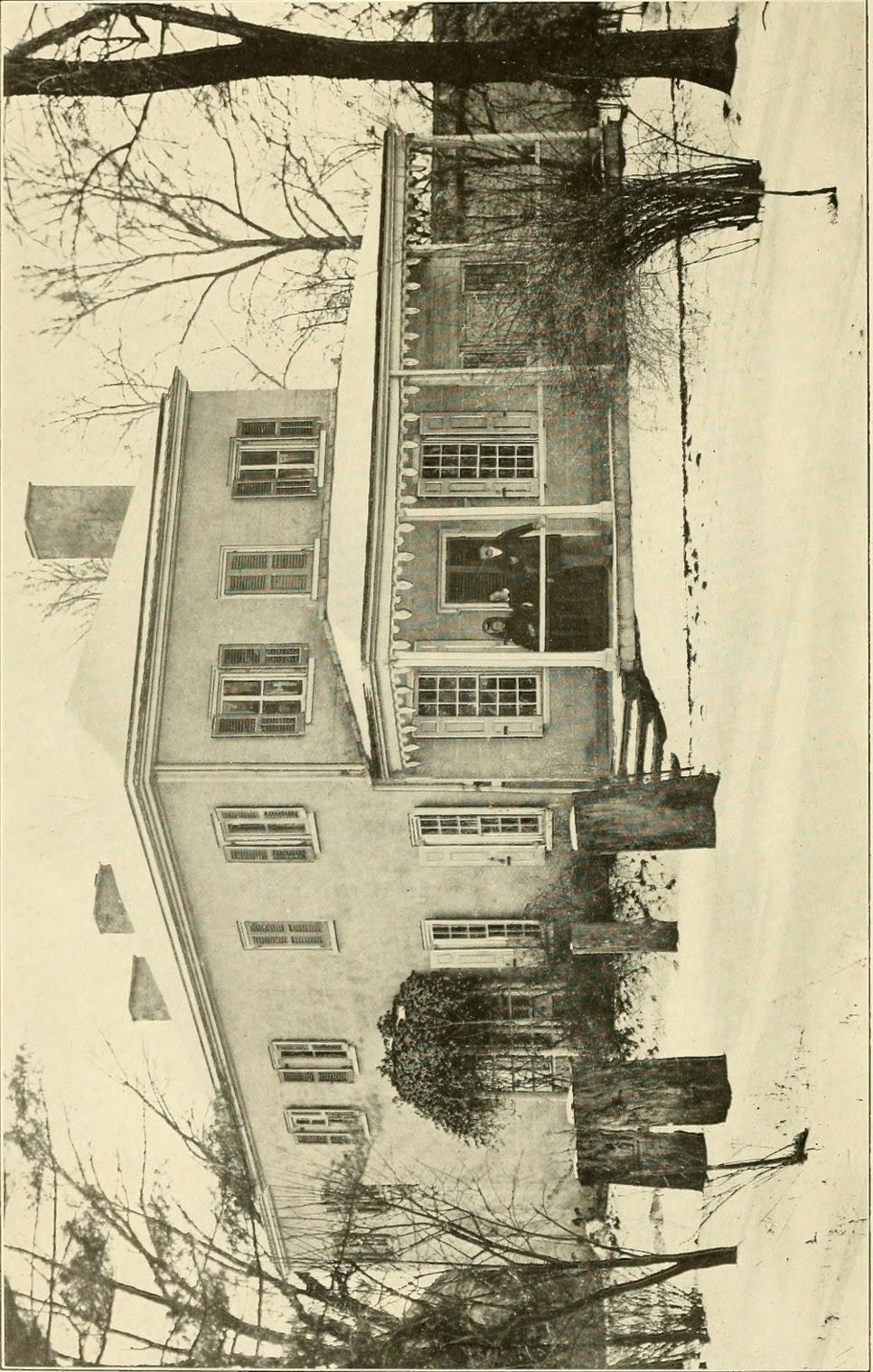
JULY, 1917

MEMORIAL VOLUME

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HISTORICAL NOTE

THE Wagner Free Institute of Science owes its establishment to the liberality and public spirit of William Wagner and his wife, Louisa Binney Wagner. In his early life Professor Wagner made extensive voyages in the service of Stephen Girard, and had opportunities to visit scientific institutions and make the acquaintance of scientific workers. He soon developed a strong interest in the natural sciences, especially geology and mineralogy, and devoted a large part of his life to studying these topics and collecting material to illustrate the teaching of them.

In 1847 he began to give free lectures at his home, near the present location of the Institute building, at that time in the rural section of the county. In 1855 the Institute was incorporated by the Legislature, a faculty was appointed and lectures were given at Commissioners' Hall, Thirteenth and Spring Garden Streets, by permission of the city authorities. In a few years the city was obliged, by its own needs, to withdraw the privilege of the hall, and Professor Wagner arranged to erect a suitable building on his own property. This was completed in May, 1865, and lectures at once given in it. In 1864 a deed of trust was executed by Professor Wagner and his wife, furnishing a permanent endowment of the Institute.

WESTBROOK FREE LECTURESHIP

By the liberality of Richard Brodhead Westbrook, D.D., for many years a trustee of the Institute, and his wife, Henrietta Payne Westbrook, provision has been made for free lectures independent of the general courses of the Institute and covering a wide range of topics.



WILLIAM WAGNER
1796-1885

FOOD FROM THE AIR

HENRY LEFFMANN

Delivered October 5, 1917

THE human being is classified as omnivorous, and this is justified not only by the common experience of mankind, but by the anatomic character of the digestive tract. The normal dental arch contains cutting, grinding and tearing teeth, the digestive secretions are adapted to all types of food, the intestinal canal is intermediate in length between those of strictly herbivorous and strictly carnivorous animals respectively.

Yet is it possible that in the earliest period man was essentially if not exclusively vegetarian. Except as to eggs and milk, the securing of animal food requires weapons and its preparation requires fire. The light that is thrown on beginnings by the tradition recorded in Genesis tends to show that pastoral life was the primitive form, that is, the rearing of animals, whose milk and eggs might have served as sources of the higher proteins. The view that all animals have the "living soul" the same as man, would be likely to give rise to a "taboo" that would prevent the general use of flesh as food. Outside of milk and eggs, primitive man may have lived upon fruits. Indeed, the idea of a "Garden" as the abode of the race, in its earliest and innocent state, expresses this view. Fruits mostly grow on perennial plants. In a balanced environment, that is, one in which reptile and bird life is allowed full play so that insect life may be controlled, such plants need no cultivation by human beings, who may simply gather the fruits as they ripen. This, as is well known, is the condition in the tropics, and inevitably leads to listlessness and indifference to the objects and methods of life, in contrast to the standards of temperate regions.

Whatever may have been the habits of human beings in the exceedingly remote past in which they were being differentiated from other primates, it is well known that the remains of the cave-dwellers and other early races show that animal food was consumed, and such practice is wide-spread today, so that with unimportant exceptions—among highly civilized people largely due to dogmas as to diet or ethical reasons—normal men and women partake freely of both classes of food, and there is no clinical or physiologic evidence that a

properly balanced ration of these is antagonistic to excellent mental and bodily health. On the other hand, it cannot be denied that abstention from animal food is consistent with equally high development of normal human powers.

It is a primary principle in biology that plants are intermediate to man and the earth. It is the plant that works up the inorganic materials, carbon dioxide, water, phosphates and nitrates, into forms, principally proteins and carbohydrates, upon which herbivorous animals feed, convert into other substances, and become in turn the food of carnivorous animals. After death, all organisms are converted into inorganic materials and the cycle of rebuilding is resumed.

It is obvious, therefore, that the maintaining of human life is absolutely dependent on maintaining vegetable life, so that in the last analysis the earth becomes the only source of wealth. The last hundred years have witnessed an enormous growth of population and its concentration in cities at an increasing rate. The area of land under active cultivation has not increased in the same ratio as the number of those who are wholly dependent on it for food and are unable to assist in such production. Statistics collected by the United States government show clearly that the production of food-animals has not kept pace with the increase of population. Altho some of the advance in the price of meats and dairy products is due to trust-control, aided by the methods of cold storage, both for withholding perishable articles and for facilitating transportation to other countries, these conditions are not alone to blame. There is a real *relative* scarcity. Moreover, the extension of sanitary control has increased the cost of production of many forms of food and diminished the return, for, as regards meats, for instance, many a carcass that formerly went to the market now goes into the fertilizer vat.

High fertility of land depends on the presence of certain classes of inorganic substances, and on certain types of living organisms. While much remains to be determined as to the best conditions of plant growth, and, indeed, it is well known that different conditions are required for different types of plants, it is now pretty well established that the plants that form part of the food of man, and of the herbivorous animals commonly eaten by him, require three types of inorganic materials: compounds of phosphorus, potassium, and nitrogen. While many forms of these compounds are capable of being utilized, a few of them are especially adapted, and it is the endeavor of the agriculturist to obtain soils in which such compounds are present or to add them if lacking. Phos-

phorus is most easily utilized when present as phosphate, nitrogen as ammonium compounds or nitrates, potassium in one of its soluble forms. In scientific agriculture large use is made of calcium phosphate, sodium nitrate or ammonium sulfate, potassium chlorid or sulfate. The extent of this use is shown by the immense quantities of "phosphate-rock" annually mined in the United States, and the fact that in normal years about 500,000 tons of potassium salts are imported from Germany and an equal amount of sodium nitrate from Chile. The deposits of phosphate-rock in our own country are so extensive that no immediate fear is felt for exhaustion, but the nitrate beds of Chile are thought to be comparatively near the end of their yield, and the dependence upon Germany for the potassium compounds gives rise to much anxiety among agriculturists in other countries.

Governmental investigations as to methods of securing supplies of nitrogen and potassium compounds have been undertaken with much vigor, and some valuable results have been obtained. So far as potassium is concerned, only brief mention is in order here. The experiments of the United States scientific stations have shown that several minerals that exist in the country in great abundance can be utilized as sources of potassium compounds, so no great anxiety need be felt on this score.

The nitrogen problem is the serious one. A great deal of attention is being given to it in civilized countries, and the war has intensified this attention, because the high explosives now used are mostly nitrogen compounds and for their manufacture require very active forms thereof. Unlike potassium and phosphorus, nitrogen does not exist in great abundance in the mineral world. The sodium nitrate deposits of Chile are almost unique. A considerable formation of potassium nitrate takes place in certain tropical countries, and by skilful treatment of decomposing organic matters nitrates can be formed, but the process is slow and but little applicable except under stress, as was the case during the French wars a century ago, when France, by reason of the British blockade, was prevented from importing nitrates for the manufacture of powder.

For a comprehension of the present phases of the food problem it is necessary to understand what is called the "nitrogen cycle," that is, the succession of associations in which nitrogen is found in nature. Strictly speaking, these associations are practically innumerable, but indication of a few distinct and easily recognizable forms will suffice for the purposes of this paper.

Beginning with the complex proteins, such as albumin and fibrin, that form the basis of living tissues, the first change is the splitting of these into somewhat simpler forms, and by successive cleavages finally into ammonium compounds, water and carbon dioxide. Most higher proteins contain sulfur and phosphorus, which are ultimately converted into sulfates and phosphates respectively, but these accessory products do not need attention here. Ammonium is converted into nitric acid, and this at once acts upon the alkaline material of the soil, calcium or magnesium carbonate, and less frequently sodium or potassium carbonate, by which nitrates are formed, which become directly the food of the higher plants, and these in turn become the food of animals, complex animal proteins are again produced, and the cycle repeated indefinitely. As these changes go on mostly under the influence of minute organisms, and as the growth and multiplication of such organisms are generally restrained by free acid, it is necessary that the soil should contain some substances capable of neutralizing the acid as fast as formed. This function is performed, as noted above, by the carbonates. Any carbonate will neutralize nitric acid, but only a few are commonly found in soil. Calcium carbonate is the most abundant. In the form of limestone it constitutes immense deposits in many parts of the world. It is but little soluble in water under ordinary conditions, but when the water contains notable amounts of carbonic acid, the solvent action is much increased. Now arable soil is rich in microbes, and the processes of the nitrogen cycle just described give rise to much carbon dioxide. This dissolves in the water percolating through the pores of the soil, and thus the calcium (and also magnesium) carbonate, otherwise but slightly soluble, can be brought into solution and readily act on the nitric acid formed by the microbes. The well-known fertility of limestone soils is explained on this principle.

The amount of nitrogen in the part of the universe with which we are acquainted is immense and much of it is in the free state in the atmosphere, which is a mixture of about four volumes of nitrogen with one volume of oxygen and small amounts of other substances, of which water and carbon dioxide are the most important. In view of possible near exhaustion of the sodium nitrate deposits of South America, and the slowness with which nitrates can be produced by ordinary methods of decomposition, agricultural chemists have for some years been turning their attention to the discovery of methods of causing the nitrogen of the atmosphere to unite with other elements so as to produce com-

pounds that may be employed for enriching the soil. These processes are also invaluable in another department of human industry, namely, the manufacture of explosives. While explosives are largely used in the destruction of life and property, they are also of the greatest value in the arts of peace. In mining, the construction of roads, tunnels, canals, the removal of river and harbor obstructions, and even in agriculture the modern high explosives are used in enormous amount. It has been discovered that by overturning the soil by dynamite a notable increase of fertility is assured. As civilized nations are impressed with the importance of both liberal food supplies and liberal supplies of explosives, there is a double incentive to discovery and invention along the line of utilization of the nitrogen of the air.

A peculiar and interesting utilization of nitrogen takes place in soil, in connection with the growth of some plants, especially those belonging to the large and widely distributed natural order, *Leguminosæ*. To this order belong several important food plants, such as peas and beans, important grazing plants, such as clover and alfalfa, and many trees, such as the honey-locust, the Kentucky coffee-tree and the acacias. The roots of many of these plants bear nodules that are collections of bacteria, which use the roots as a physical support and which carry on processes by which nitrogen is fixed and rendered available for the use of the host plant. This is not a true parasitism, but more like a mutual relationship, and hence it is known to the biologist as "symbiosis" (joint life). It has long been known that the fertility of land can be materially increased by planting clover, and, after it has reached good growth, plowing it in. The reason for this effect is now understood. It appears that each species of leguminous plant is best served by a particular species of micro-organism. It is now a practice to inoculate the seeds of such plants with pure cultures of the appropriate organism and thus increase the yield.

These processes of nitrogen-fixing are slow and can be applied only to farming areas and made applicable only to certain crops, except indirectly. The nitrogen compounds must be utilized in the place in which they are produced for the growth of plants, so that one very important application of fixed nitrogen, that for the manufacture of explosives, is not met by this method, hence chemists have been seeking energetically of late years for methods of nitrogen-fixation available under a great variety of conditions and in many locations.

FIXATION OF NITROGEN BY OXIDATION

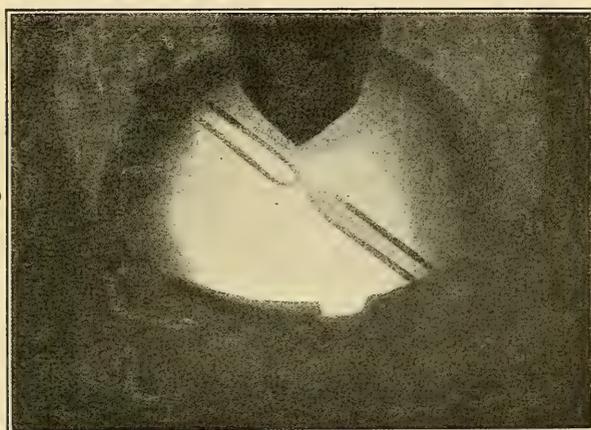
The element nitrogen ordinarily shows in the free state very low chemical affinity. It was, indeed, formerly considered as one of the most indifferent of elements, but research has brought to light a few elements—gases at ordinary temperatures and existing in small amount in the air—which are apparently without chemical affinity. Free nitrogen combines directly even under the influence of high temperature with but few elements, one of which is magnesium. Under the influence of the electric spark direct combination of the nitrogen and oxygen of the atmosphere can be secured. This was discovered in the 18th century, in the course of researches by Henry Cavendish and Joseph Priestley. Whether the combination is due to the increase of the affinity of the nitrogen or the oxygen or both, is not definitely known and is not important here. It is known that pure oxygen can be converted by electric discharges, especially the so-called “silent discharge,” into a much more highly active form without an alteration in fundamental composition. This form, termed “ozone,” manifests itself by a distinct odor and by oxidizing readily many substances—*e. g.*, silver—upon which ordinary oxygen has no action. Evidence of the production of ozone is noted almost always when electric discharges are occurring, whether these be silent or noisy and whether spark or arc, but the amount of ozone produced is so much dependent on the form of the discharge that in practice both for making ozone as such and for oxidizing nitrogen only certain forms are used.

Cavendish used the spark of a static machine, and some modern apparatus for producing ozone use discharges of high voltage currents either through a special dielectric or directly through dry air. For nitrogen-fixation on a commercial scale, processes entitled to consideration here are three in number, of which one is direct oxidation and the others direct combinations of other types.

The direct oxidation has been carried out in several ways, but present usage is limited to the employment of a flaming arc. The earlier experiments were made with electrodes drawn so far apart as to make the arc unsteady, but the modern forms do not apply this principle.

One of the best known, and apparently most successful, forms of apparatus for direct oxidation of nitrogen is the Birkeland-Eyde furnace which depends on developing an arc by an alternating current of high voltage in a constant magnetic field. The furnace is usually a sheet-steel drum about eight feet in

outside diameter, lined with very refractory material, leaving a cylindrical space in the center. Air is supplied by any convenient blower, and the products pass out by special openings to the condensing or absorbing vessels. The electrodes are U-shaped copper tubes, the curve being tipped with the poles. Water circulates constantly through the tubes. The points of the electrodes are within a strong magnetic field by the action of which the arc is spread out in the form of a fan on each electrode. In an apparatus of the dimensions noted above the arc will be about six feet in diameter. Interesting electric phenomena are noted during the running of the furnace, but these do not require discussion here. The operation of the furnace involves severe action on the materials with which it is lined, and renewals have to be made frequently.



Arc of the Birkeland-Eyde furnace. From *Trans. Far. Soc.*, 1906, 2, 98.

A plant operating on the general principle of the Birkeland-Eyde apparatus was installed by Bradley and Lovejoy, near Niagara Falls, deriving electric power from that point, but it was apparently not commercially successful, as it was discontinued in 1904. In normal conditions, heretofore, the abundance of sodium nitrate and the ease with which it may be imported into the United States have rendered methods of nitrogen-fixation unprofitable, but conditions in these respects threaten to change very much and it behooves Americans to give earnest attention to the application and development of such procedures.

Another form of nitrogen-oxidizing furnace is that devised by Schoenherr. It is essentially a long tube into which an iron rod enters at the lower end, con-

stituting one electrode, and an iron pipe extending some distance up the tube, the other electrode. Air at a temperature of about 500° is admitted at considerable pressure near the lower electrode and causes the arc to be elongated, and also carries the products of oxidation up the tube to a cooling chamber, from which they are taken to the absorbing liquid.

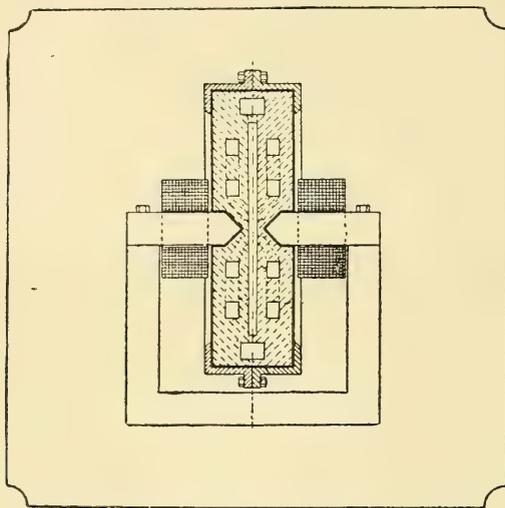


Diagram of Birkeland-Eyde furnace. *Trans. Far. Soc.*, 1906, 2, 98.

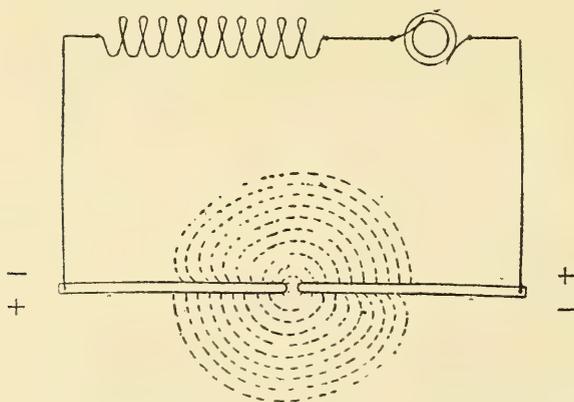


Diagram of arc of Birkeland-Eyde furnace. *Trans. Far. Soc.*, 1906, 2, 98.

The combination of oxygen with nitrogen in these and similar forms of apparatus usually involves careful regulation of the temperature, as the reactions are of the type termed "reversible," that is, decomposition into free nitrogen and oxygen will take place almost as rapidly as combination. Nernst

and Jellinek found, however, that inasmuch as the combination (resulting in the formation of nitric acid) is "endothermic," that is, accompanied by absorption of heat, it is favored by the high temperature of the gases, and they found, further, that if the products are cooled quickly, the reversion that occurs at the lower temperatures can be prevented. Nitric oxid is stable at temperatures below 1000° , hence the conditions of efficiency in these processes are to combine the substances at a very high temperature and cool the products as quickly as possible to at least 1000° . To secure the high temperature necessary for combination, no method other than the electric arc is yet available practically. As arcs can easily be obtained at low cost by water-power, the operation of such plants has been especially developed in mountainous countries, such as Switzerland and Scandinavia. Abundant opportunities for such development exist in the United States.

The action of the arc is not entirely by its heat, for, as noted above in connection with Cavendish's experiments, a direct exaltation of the chemical affinity of the oxygen takes place. If an electric discharge is passed thru pure dry oxygen, a diminution of volume occurs and ozone is produced.

FIXATION OF NITROGEN BY ABSORPTION

Calcium carbid, produced by the action of finely divided carbon (coal or coke) upon lime under the influence of the electric arc, has been manufactured for many years in large amount for the production of acetylene. When it is heated to about 1000° in a current of nitrogen, direct combination takes place, with the formation of calcium cyanamid, CaN_2C , the reaction being $\text{CaC}_2 + \text{N}_2 \rightarrow \text{CaN}_2\text{C} + \text{C}$.

Calcium cyanamid may be used directly as a fertilizer, and as it contains about four per cent. more of available nitrogen than sodium nitrate, it is being prepared on a very large scale. For the production of calcium cyanamid, the carbid must be in a fine state of division. To prevent accidents from evolution of acetylene, in consequence of the action of moisture, the final grinding is carried out in an atmosphere of nitrogen. The process is carried out either by heating the carbid by means of an electric arc within the mass, or in retorts by direct outside firing.

Unlike the combination of nitrogen and oxygen, which is endothermic, the action of nitrogen on calcium carbid is "exothermic," that is, attended

with production of heat, hence the temperature increases. Care must be taken that this increase does not go beyond 1400° , as the reaction, like that of the oxidation of nitrogen, is reversible, and the cyanamid will be decomposed.

The electric method has some advantages over that by heating in retorts. The combination once begun is carried on by the heat produced in the reaction, hence the current may be cut off. Superheating is not likely to occur and the action proceeds from without inward, which causes the product to shrink from the walls of the containers.

On the large scale, as at Odda, Norway, the process requires about thirty hours.

At several plants on the continent of Europe the direct heating process is used, but some practical difficulties have developed. The most serious is that the heating cannot be so easily controlled and hence loss of cyanamid may occur, also the mass adheres to the walls of the retorts and has to be hacked out. It has been found that the addition of moderate amounts of calcium chlorid or calcium fluorid will diminish these conditions. These substances appear to act especially by reducing the temperature necessary for the action, probably by rendering the carbid fusible at a lower temperature. The product of this modified method contains some calcium chlorid, which makes it liable to absorb moisture—a notable disadvantage.

Calcium cyanamid is marketed in a finely powdered form, often under the term "nitrolim."

It will be seen that the cyanamid processes differ from the nitrogen-oxidation processes by the fact that the former require practically pure nitrogen, at least, nitrogen with no appreciable amount of oxidizing substances or moisture. In the oxidation processes the raw material is air, which is obtainable in unlimited amount. The production of the pure nitrogen necessary for the cyanamid method is largely by the liquefaction of air and separation of the nitrogen and oxygen by fractional evaporation. In some works the nitrogen is obtained by passing air over hot copper, by which the oxygen is removed. The copper is then recovered by heating the oxid in a current of water-gas.

Improved air-liquefaction methods yield nitrogen containing not over 0.1 per cent. of oxygen.

The fertilizing action of calcium cyanamid is dependent essentially upon its power of yielding ammonium compounds under the influence of moisture, with probably the coincident action of soil bacteria. Several stages of the

reaction may occur, but the final result is expressed by the equation $\text{CaN}_2\text{C} + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CaCO}_3$.

From this reaction it is obvious that the material may be used as a source of ammonium compounds. For this purpose it is acted upon by superheated steam. Other derivatives of calcium cyanamid find application in color and explosives industries that do not need consideration here.

FIXATION OF NITROGEN AS AMMONIA

Many sources of ammonium compounds are available. They are found in notable amount in the products of the putrefaction and destructive distillation of many animal and vegetable materials. In these cases they are the result of decomposition of nitrogenous substances by complex reactions almost wholly unknown, and as they do not involve the fixation of atmospheric nitrogen, do not come within the scope of this essay.

As ammonium compounds can be transformed into many other forms with comparative ease, their abundant supply is desirable, hence much attention has been given to utilization, for their production, of the immense stores of nitrogen in the atmosphere.

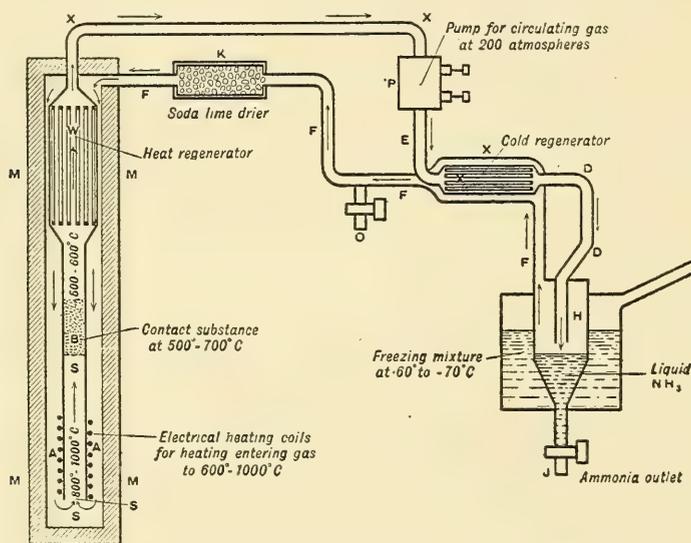
For their production by the direct action of nitrogen and hydrogen (synthetic ammonia) the two gases in a high state of purity are obtained by well-known industrial methods. Their union is accomplished by the joint action of heat, pressure, and a catalyst. The last mentioned is a substance that promotes combination without permanently entering into the compound formed, hence a small amount of it will suffice to bring about combination of large amounts of the other substances.

The combination of nitrogen and hydrogen in pure dry condition gives ammonia, NH_3 , which is readily absorbed by water and acids. The volume of ammonia is less than that of the free gases (a mixture of one volume of nitrogen and three volumes of hydrogen produces two volumes of ammonia). The reduction of volume causes the reaction to be favored by pressure.

The scientific and practical investigation of the production of synthetic ammonia is due to Haber and Le Rossignol, who in 1913 published a paper in *Zeit. f. Elektrochemie*. They found that by employing a pressure of about 200 atmospheres (3000 pounds to the square inch), a temperature of between 500° and 700° and passing the gases over a catalyst, from three to twelve per cent. of ammonia could be obtained.

The details of the most recent practical application of this method have been withheld almost entirely owing to the fact that it has been operated in Germany, and the data concealed on account of the war. It is known that a large plant was erected near Ludwigshafen by the *Badische Anilin und Soda Fabrik*, and it is stated by Gilbert (see bibliography) that the latest report gave 200,000 tons of ammonium sulfate as a year's output. This corresponds to about 50,000 tons of synthetic ammonia.

The choice of catalyst is limited. Haber and Le Rossignol found osmium the most active of those they tried, but its high cost is a serious ob-



Haber & Le Rossignol process for synthetic ammonia.
Martin & Barbour. *Industrial Nitrogen Compounds*, 54.

jection. It has fortunately been found that commercial metallic uranium will act very well. The enormous pressure required introduced practical difficulties which have been overcome by very careful construction of the pressure containers and, it is stated, avoiding the dangers of explosion by burying these in the ground.

As large amounts of heat and mechanical energy are not required for this process, it is capable of exploitation in many parts of the world, not being confined to districts in which cheap water-power is available.

The annexed diagrammatic illustration will show the general method. For reasons noted above, information as to exact construction and operation

of the German plants is not available. The ammonia produced may be converted in any ammonium compound (the sulfate is very largely produced) or oxidized into nitric acid.

Gilbert regards the process as not having yet shown high practical value, and as not likely to be extensively applicable in the United States.

The production of nitric acid by the oxidation of ammonia deserves brief notice. This takes place under the influence of a catalyst, the best being, so far as known, smooth solid platinum. Certain specified conditions must be maintained or a reaction liberating nitrogen will occur. The reaction desired is $\text{NH}_3 + \text{O}_4 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$. Other catalysts have been discovered, among which is a mixture of ceria and thoria, somewhat similar to that used in the Welsbach mantle. This is cheaper than platinum, especially at the present time, but is not so efficient. A German patent covers the use of a mixture of roasted iron pyrites and copper oxid—which may possibly be obtained by roasting the common copper pyrites—claiming that under this influence nitrous anhydrid, N_2O_3 , is formed readily from a mixture of ammonia and oxygen.

There is no question that the methods of increasing the supply of nitrogen compounds, particularly the utilization of atmospheric nitrogen, are of the greatest importance to civilized nations. The stress under which the *entente* powers of western Europe, especially Great Britain, have been placed in consequence of inability to secure within their own borders sufficient food and explosives, thus forcing dependence upon sea-borne traffic, now most seriously threatened by the submarines of the central powers, indicates the peril of all nations that neglect to provide for abundant plant food.

Gilbert (see bibliography), writing in the early part of 1916, thus summarizes the condition and prospects of the several methods.

Nitrogenous compounds are essential not only for the manufacture of explosives, but to maintain the country's capacity for self-support. To be effective, the source must be such that the products may be adaptable to either requirement.

The arc method has not thus far demonstrated capacity to meet the agricultural requirement at all or even the defense requirement efficiently.

Definite knowledge concerning the Haber (synthetic ammonia) process is lacking, but the record of achievement is against it and it would seem unsuited to American conditions, at least in the present state of its development:

The cyanamid process is capable of development which will meet the requirements for a cheapened nitrogenous fertilizer source whose form of nitrogen content is readily converted into nitric acid. The process is already a prominent factor in the economic well-being of most countries of the older civilization, and is capable of similar extension in the United States.

Gilbert bases his doubt as to the value of the Haber process on the fact that it "involves technical difficulties in the way of manipulation which have prevented the proportionate extension of its use, even in Germany, . . . where cheap skilled labor and military exigency have combined to give every advantage over conditions in this country." The history of industrial processes, however, gives ample evidence of the capacity of human ingenuity by "patient search and vigil long" of overcoming technical difficulties, reducing working costs, and securing better and larger yields.

NOTE.—At the time this lecture was delivered, the processes of nitrogen-fixation devised by Professor John F. Bucher had not been announced. They are described in connection with Dr. Horn's lecture on "Catalysis in the Inorganic Field."

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The following are recent publications in English which have been used in the preparation of this essay and from which a large amount of data may be obtained by any one specially interested in this important topic.

The Manufacture of Nitrates from the Atmosphere. *Ernest Kilburn Scott*. Smithsonian Institution Report for 1913, reprinted as a separate pamphlet, Publication 2291, Government Printing Office, Washington, D. C.

Sources of Nitrogen Compounds in the United States. *Chester G. Gilbert*. Smithsonian Institution, Publication 2421. Published by the Institution.

Industrial Nitrogen Compounds and Explosives. *Geoffrey Martin & William Barbour*. 8vo, 117 pages and indexes. D. Appleton & Co., N. Y. 1915. Extensive references to the literature will be found in this work.

The article by A. W. Crossley, on "Utilization of Atmospheric Nitrogen" in Thorpe's *Dict. App. Chem.* 3, should also be consulted.

THE ELIMINATION OF GRADE-CROSSINGS IN CITIES

SAMUEL TOBIAS WAGNER

Delivered February 1, 1917

A GRADE-CROSSING is generally understood to mean the crossing of a railroad by a highway when both are at the same level. The same term is applied to the crossing of one railroad by another at the same level. It is never understood to apply to the situation of a pedestrian crossing the driveway of a road or street on which vehicular traffic passes, but in a broad sense this is also a grade-crossing. All are dangerous and should be eliminated if possible.

The present discussion is confined to the crossing of a railroad and a highway. It is possible to control the movements of trains where two railroads cross each other, by what are known as interlocking signals, which are so arranged mechanically that the danger of a collision is reduced to a minimum. On the other hand, the best possible protection that can be devised for a highway crossing can be defeated by reckless or careless travelers on the highway, who cannot be controlled by any mechanical device, who are unwilling to heed the warning to "Stop, Look and Listen," and will dodge under safety gates into the path of trains approaching in plain sight, or will even drive their automobiles through safety gates or past a watchman trying to stop them, into the sides of moving engines or trains.

It is therefore necessary, at specially dangerous crossings, to provide an absolute separation of the railroad from the highway by having one pass over the other.

I. HISTORY

The existence of grade-crossings is a necessary evil. When railroads were first constructed, in places where the grade-crossing is now in existence, there was no other way in which many of them could have been built. At the time the railroads were built neither the railroads nor the communities which have grown into towns and finally into cities would have been able to stand the expense of construction, which would have avoided the crossings at grade, and

their existence was, therefore, an economic necessity. If they had been required at that time, it is likely the railroad could not have been built. As the travel on the railroads and highways increases, these crossings become more and more objectionable. Some system of protection by means of watchmen and gates is then required, and finally nothing remains to be done but to eliminate them altogether at great expense. In the study of any particular case we will find that the necessity of opening more streets over the railroad, as the city develops, makes conditions worse. Neither the railroad nor the city is independent of each other; their interests are mutual. One depends on the other for its increase of business or for its extension and development. The final situation which calls for action is one of necessity, in which both interests are involved, and the measure of the necessity is the amount and character of the traffic, the amount of interference with travel, and the amount of danger. It may be that the amount of traffic on the railroad or street is such as to call for some kind of protection or the regulation of the speed of trains, but this soon ceases to be adequate and a point is reached when the expense of the elimination of the crossing is justified.

The history of the work of the systematic elimination of grade-crossings possibly extends back to about the year 1880, although it did not begin to be considered an important subject until within the past twenty years. During the past fifteen years the progress has been steady, and the movement toward the elimination of the most dangerous ones has been rapid on the part of the cities and the railroads.

The greatest work in this line has probably been done in the city of Chicago, where, on account of the level character of the ground and the large number of railroads, the conditions are worse than in almost any of the large cities in the United States. It is stated that the elimination of 780 grade-crossings had been arranged for in Chicago up to 1911. Philadelphia is credited with the next largest number, viz., 120, and Buffalo third, with 94 to its credit.

2. PROTECTION WITHOUT ABOLISHMENT

Except as to those reckless or careless travelers on the highway who will pay no attention to any warning, grade-crossings can be protected so that they may safely be used.

In many cases a crossing can be protected so as to make it fairly safe except for those who will pay no attention to any warning. A list of the various

methods of grade-crossings protection is given by *The Railway Review* of May 27, 1916, the methods being given in the order of their effectiveness:

1. Gates operated day and night.
2. Crossing flagmen day and night.
3. Gates by day and automatic bell by night.
4. Crossing flagmen by day and automatic bell at night.
5. Crossing flagmen by day and unprotected at night.
6. Automatic devices only, such as crossing alarm bell or automatic flagmen.
7. Crossing unprotected save by signs.

It is interesting in this connection to note some of the data which have been collected to determine the attention which is paid by the public in passing over a grade-crossing.

Observations were made at the various crossings of the Baltimore and Ohio South Western Railroad in Ohio and Indiana in February and March, 1914. (Proceedings A. R. E. A., 1915, Part 2, Monographs, p. 178.) These are given in Table 1.

TABLE 1
OBSERVATIONS AT GRADE-CROSSINGS OF THE B. & O. S. W. R. R. IN OHIO AND INDIANA
February and March, 1914

	PEDESTRIANS	TEAMS	AUTOS	TOTAL
Stopped and looked both ways	none	none	48 5%	48
Kept moving and looked both ways	2,897 12%	796 17%	125 13%	3,818
Kept moving and looked one way	4,645 19%	764 17%	152 16%	5,561
Kept moving and looked straight ahead	17,356 69%	3,021 66%	626 66%	21,010
Total	24,908	4,581	951	30,437

From this table it is easy to determine how many people crossing over railroad tracks fail to observe the law to "Stop, Look and Listen."

The Pennsylvania Railroad Company has published a statement of all accidents which happened on their lines east of Pittsburgh, between January and August, 1916, inclusive. This list is given in Table 2.

TRANSACTIONS OF WAGNER
THE ELIMINATION OF GRADE-CROSSINGS IN CITIES

TABLE 2

THE PENNSYLVANIA RAILROAD COMPANY—INSURANCE DEPARTMENT. INJURY
TO PASSENGERS AND OTHERS (EXCLUDING EMPLOYEES). STATEMENT OF
ACCIDENTS AT GRADE-CROSSINGS, INVOLVING PERSONS KILLED AND IN-
JURED

January to August, Inc., 1916

LINES EAST OF PITTSBURGH

GRADE-CROSSINGS	ACCIDENTS	KILLED	INJURED
Automobiles struck by trains	45	26	77
Bicycles struck by trains	2	..	2
Motorcycles struck by trains	1	..	1
Teams struck by trains	54	21	46
Trolley cars struck by trains
Foot travelers struck by trains	25	15	10
Trespassers struck by trains, due to going under or around gates when down	8	2	6
Automobiles running into side of trains	14	3	39
Bicycles running into side of trains	1	..	1
Motorcycles running into side of trains	6	1	7
Teams running into side of trains	2	1	2
Trolley cars running into side of trains
Foot travelers walking into side of trains
Automobiles running into safety gates	5	..	6
Bicycles running into safety gates
Motorcycles running into safety gates	5	..	7
Teams running into safety gates	2	..	3
Trolley cars running into safety gates
Foot travelers walking into safety gates	2	..	2
Automobiles struck by safety gates	6	..	10
Bicycles struck by safety gates
Motorcycles struck by safety gates
Teams struck by safety gates	3	..	3
Trolley cars struck by safety gates
Foot travelers struck by safety gates	12	..	12
Trespassers—fell or caught between cars while climbing over trains at crossings	5	1	4
Total	198	70	238

This table shows in a very clear manner the various ways in which grade-crossing accidents occur. In examining this list it appears that the greatest number of accidents occur in the following manner:

1. Teams struck by trains, 54.
2. Automobiles struck by trains, 45.
3. Foot travelers struck by trains, 25.
4. Automobiles running into side of trains, 14.

It is also interesting to note that there were no accidents of any nature to trolley cars. Attention is also called to the fact that 37 accidents were due to running into the side of trains or into safety gates.

The Long Island Railroad Company recently issued a placard which reads as follows:

TO AUTOMOBILE OWNERS AND CHAUFFEURS

The moral the Long Island Railroad is trying to point out in its campaign against reckless automobile driving over grade-crossings is this:

It is better to wait at a railroad crossing than at a doctor's office.

The only sure way to avoid being struck by a train is to **STOP BEFORE YOU CROSS.**

This Company has spent \$15,000,000 eliminating 305 crossings. It spends \$25,000 a month—\$300,000 a year—to protect those crossings that still exist.

We are doing our part. Won't you do yours?

In order to show that under present traffic conditions in large cities the danger to pedestrians is not confined to railroad crossings at grade, the data given in Table 3 are enlightening:

TABLE 3

COMPARISON OF CASUALTIES TO PERSONS AT GRADE-CROSSINGS OF RAILROADS AND STREETS, WITH CASUALTIES TO PEDESTRIANS WHO WERE STRUCK OR RUN OVER BY VEHICLES ON STREETS IN CHICAGO

YEAR	GRADE-CROSSING ACCIDENTS		RUN OVER OR STRUCK BY VEHICLES	
	NO. KILLED	NO. INJURED	NO. KILLED	NO. INJURED
1905	99	48	34	602
1906	68	65	45	643
1907	38	62	48	774
1908	20	27	53	878
1909	33	63	57	1124
1910	48	96	52*	946*
1911	20	72	103	1843
1912	37	107	75	2530
1913	54	77	86	3012
1914	31	111	143	3455

The above list does not include street cars.

* Record is for automobiles only.

Railway Age Gazette, October 8, 1915.

This table shows that about five times as many people were killed in Chicago in crossing ordinary streets in 1914, and thirty times as many injured as there were at railroad grade-crossings. It would, therefore, seem that, in

Chicago, it is safer to cross a railroad grade-crossing than an ordinary street. Without data of this kind such a statement would seem incredible.

The Annual Report of the Public Service Commission of Pennsylvania gives the following statistics as to the casualties at railroad grade-crossings in Pennsylvania for the year ending June 30, 1916.

Pennsylvania has 11,776 grade-crossings, of which 1,794 are protected. This represents fifteen per cent. of the whole number. On these crossings in the past year 161 persons were killed and 357 injured. The Commission states that it will cost \$10,000,000 to complete grade-crossing work now pending, not including those in Philadelphia.

The Pennsylvania recently exhibited the following placard:

WHAT THE PENNSYLVANIA RAILROAD SYSTEM HAS DONE

There remain on the 11,000 miles of the line comprising the Pennsylvania System, 13,027 crossings at grade. It costs an average of at least \$50,000 to remove a grade-crossing. Thus to eliminate every such crossing on the lines of this system would cost upward of \$600,000,000. The various companies of this system have, since 1902, expended \$66,641,294 in improvements resulting in the elimination of 1052 grade-crossings.

AN APPEAL TO THE PUBLIC

Grade-crossings are unavoidable. Without them few railroads could have been built in this country. They are one of the inconveniences of progress, to be eliminated just as fast as possible. Railroad officers are doing their best but it all takes time and money.

Meanwhile the public demands that trains be run on time. To do so involves speed over crossings. The railroad appeals to the driver of every vehicle to "Stop, Look and Listen." A little care and a momentary stop may mean the saving of a human life.

Human lives are the most precious things in the world.

3. HOW GRADE-CROSSINGS CAN BE ABOLISHED

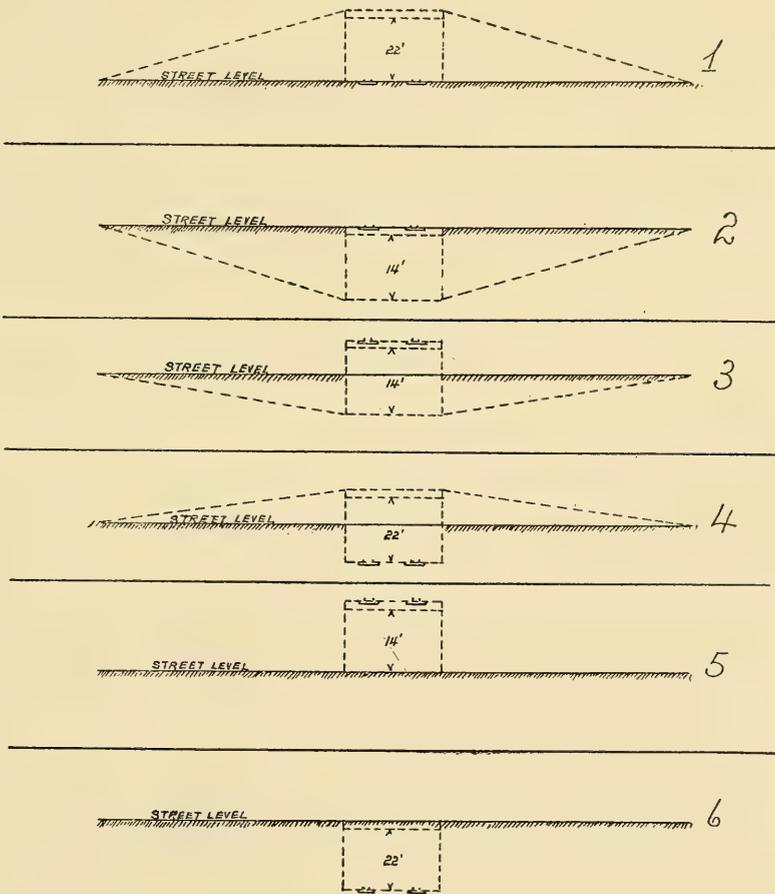
In the most general way there are six methods by which a grade-crossing can be done away with:

1. Raising the street over the railroad.

2. Lowering the street under the railroad.
3. Lowering the street and raising the railroad.
4. Raising the street and lowering the railroad.
5. Raising the railroad over the street.
6. Lowering the railroad under the street.

These methods are shown in a diagrammatic manner in Table 4.

TABLE 4



By an examination of these methods the changes required to the railroad are a minimum in 1 and 2, and increase in the order given, while exactly the reverse holds good when the changes required for the street are considered. It would also seem that, other considerations being equal, 3 and 4 would affect the railroad and the street equally.

In all these cases it is evident that either the street or the railroad must increase its rate of grade, and this single point is generally the most difficult one to deal with in any particular case. The increase in the rate of grade of a railroad is always accompanied by loss of revenue. On a street it is difficult to calculate actual money loss by increasing the grade.

To obtain light grades on a street means expensive first cost, when the street is lined with expensive properties requiring to be adjusted to the new conditions. The consequential damages which may be recovered by law for such changes are often a very large part of the total cost of the work. It is evident that the only cases in which there are no consequential damages due to changes of grade of the street are in 5 and 6.

Unfortunately, the elimination of such crossings is not profitable to either the city or the railroad from a financial standpoint. Neither can expect to receive any financial return for the large amounts which must be expended. The railroad will save in not having to protect the crossing with gates and watchmen, and will be relieved from maintaining the crossing, but, on the other hand, it is called upon to maintain expensive bridges, etc., with their painting and waterproofing. For instance, on the Ninth Street Elevated of the Philadelphia & Reading Railway in Philadelphia, there are eight and one-quarter acres of solid steel floor bridges to be painted and maintained. This is a cost which must be met for all time. Further, when these steel structures have run their lifetime, which is not likely to be more than thirty years, they must be replaced. It is obvious, therefore, that the saving from watchmen's wages and the cost of maintaining gates is trivial as compared with the interest on the enormous sum required to build such elevated steel structures, the greatly increased cost of maintenance as compared with the cost of maintaining a railroad at the ground level, and the cost of replacement.

It has been claimed that, by the elimination of grade-crossings, the railroads will save expense by avoiding the damages for grade-crossing accidents. It can be shown that in the majority of such cases the accidents are due to what is known as "contributory negligence," that is, that the person so injured has not "stopped, looked or listened," as required by law, or has done something contributing to the accident.

In these days, when the attention of the public is so constantly directed toward grade-crossing accidents, which, in the great majority of cases, are due to the reckless disregard by travelers on the highway, or automobilists, of all

the means of protection that can be devised for their safety, it is not uncommon to find the view expressed by some public authorities or by newspaper writers that it is the duty of railroad companies absolutely to prevent accidents at grade-crossings, and it is often assumed that the railroad company would save money by eliminating grade-crossings. All fair-minded persons will assent to the proposition that, when a railroad company has adopted standard means of protection at a grade-crossing and an accident occurs through refusal of travelers to heed the warnings given by automatic bells, watchmen, or safety gates, the railroad company is not responsible, legally or morally, for the consequences of the accident, however sad or regrettable it may be. Railroad managements, however, from motives of humanity, in order to prevent the accidents that experience has shown occur with frequency at certain crossings through the recklessness of travelers on the highway, are generally willing to spend, for the elimination of such crossings, large sums of money, which they know will be absolutely unproductive, when any reasonable terms can be made with the public authorities.

Another item, not usually considered, is the loss of revenue to the railroad from business along the changed line. In thickly settled communities the profitable business of the railroad is largely dependent upon the number of industrial connections to the railroad, such as manufactories, coal-yards, etc. The elevation or depression of the tracks due to the elimination of the grade-crossings causes the severance of a large number of these connections, many of which can never be reconnected. This results in a large loss of business. In the city of Philadelphia, on the Reading System, Table 5 shows the number of these connections before and after the work of abolishing the grade-crossings:

TABLE 5
INDUSTRIAL CONNECTIONS BEFORE AND AFTER ELIMINATION OF GRADE-CROSSINGS IN PHILADELPHIA

LOCATION	BEFORE	AFTER
P. & R. Ninth Street Elevated	95	42
Richmond Branch Elevated	17	9
Pennsylvania Avenue Subway	29	26

Not only does the railroad suffer a loss of revenue from the severing of these connections, but the properties themselves are frequently placed in such a position as to curtail their future usefulness, which is a public detriment.

From the city standpoint, the whole territory adjacent to a crossing which has been eliminated by carrying the highway over or under the railroad derives a very substantial benefit, although properties in the immediate vicinity may sustain serious damage from the change of grade of the highway. When the grades of streets are radically changed, the damages resulting to owners of private property, not of an industrial character, may be very serious, even assuming that they recover all that is possible by due process of law.

When tracks or streets are seriously depressed below the existing surface, great expense is caused by the necessity for proper drainage, the lowering of water and gas pipes, electric conduits, etc. On the Pennsylvania Avenue Subway—Reading System—in Philadelphia, where the tracks were depressed below the street surface, the cost of the drainage alone amounted to over \$500,000 in a total cost of \$5,500,000.

In the depression of railroads or streets the danger and expense to adjacent buildings caused by excavating below their foundations are serious matters, and in the case of railroads the difficulty of reestablishing industrial connections is great and expensive.

Frequently also the right of way of the railroad is inadequate to either elevate or depress the tracks without incurring greatly increased cost to maintain travel during the process of reconstruction. In some cases this is a matter that causes much loss of revenue during the time of reconstruction, especially when the time is long. During the time that a street is being depressed the inconvenience and damage to business interests are great and not fully covered by damages recoverable by law.

From the city standpoint the depression of the tracks is often preferable if it allows the streets to remain in their original elevation, as it causes much less general disfigurement. A subway is preferable for this reason to an elevated, although the cost is always very much greater. Just what method should be adopted must be carefully studied for each individual case and no general rules can be laid down.

4. LEGISLATION AND DIVISION OF COST

No complete compilation has ever been made showing the practice required by the several States where grade-crossing elimination has been carried out. In 1913 an investigation was made by the St. Louis Public Library Monthly Bulletin for July (Proceedings A. R. E. A., 1915, Part 2, Monographs),

in which the following conclusions are drawn from investigations made in thirty-nine cities in the United States:

“The tendency seems to be to keep at least a part of the authority in the matter of grade-crossing elimination in the hands of the State. Recent legislation, like that in New Jersey, tends to vest the State Public Service or Public Utilities Commission with the necessary powers. This is also the case in New York, Connecticut, Massachusetts, Wisconsin and California. ‘Home Rule’ in grade-crossing elimination does not seem to be as fashionable as might be expected. In a great many cases the State has passed enabling acts that municipalities may pass ordinances providing for crossing separation; but here, in many cases, as in Ohio, the apportionment of cost is fixed by the State law. Other cities, like Providence, are powerless to act without special State law in each specific improvement. The most liberal State legislation may be found in the case of special acts applying to Buffalo, whereby the city may enter into any sort of contract it pleases. These special acts cover only certain specified though comprehensive improvements, and further legislation must be sought from time to time.

“Chicago appears to be able to do as it likes in the matter of grade-crossing work. Special ordinances are passed for all improvements. Philadelphia and Pittsburgh are unhampered by any State limitations. A great deal has been accomplished in these cities, but the general tendency throughout the country seems to be toward uniform State legislation.

“The apportionment of the cost is, of course, the great question in grade-crossing elimination work. In some of our most progressive cities this is fixed by law—usually State law. In thirteen of the cities investigated this is the case. Massachusetts cities must, unless special legislation is passed, pay not over ten per cent. of the total. Connecticut cities pay nothing, twenty-five or fifty per cent., depending on who brings the petition, and upon priority of the existence of the railroad or highway. New York cities, except Buffalo, must pay twenty-five per cent.; Ohio cities, thirty-five per cent. The drastic New Jersey law puts practically no expense on the city. In New York, Massachusetts and sometimes Connecticut, the State meets a portion of the expense, in the first two named States, twenty-five per cent.”

The adjustments made in the city of Philadelphia in a number of large grade-crossing eliminations are shown in Table 6:

TABLE 6

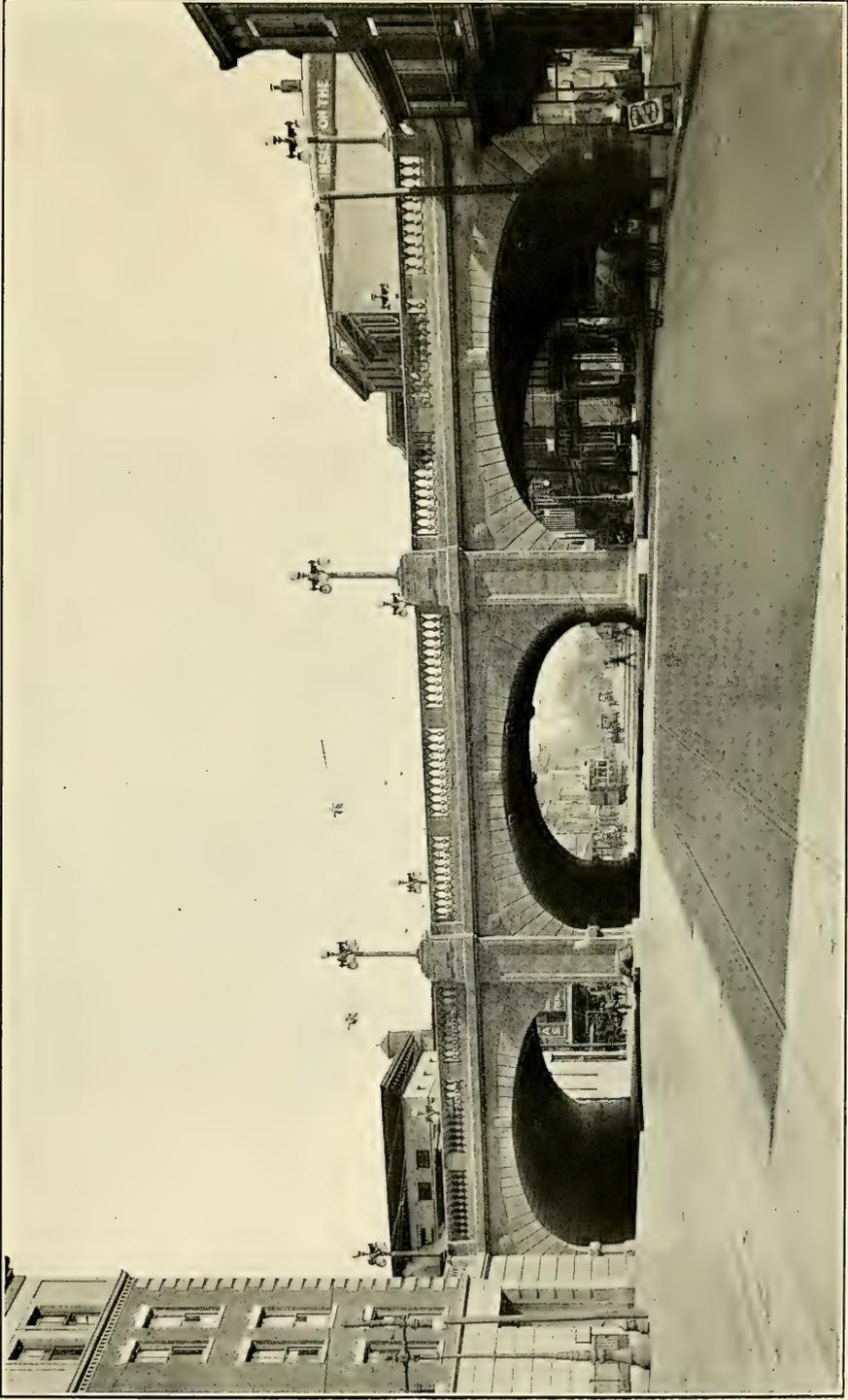
DIVISION OF COST, ELIMINATION OF GRADE-CROSSINGS IN PHILADELPHIA

YEAR	LOCATION	RAILROAD'S SHARE	CITY'S SHARE
1892	Penna. R. R. (Connecting R. R. & North Penn. R. R.)	\$100,000	\$200,000
1894	P. & R. (Pennsylvania Ave. Subway)	2,750,000	2,750,000
1897	Penna. R. R. (Phila. & Trenton)	1,250,000	750,000
1900	P. & R. (Chestnut Hill Branch)	146,000	70,000
1906	P. & R. (Main Line & Rich. Branch)	5,000,000	5,000,000
1916	Penna. R. R. & B. & O. (So. Phila.)	14,760,000	9,900,000

It is of frequent occurrence that when one grade-crossing in a city has to be eliminated, it carries with it a number of others on account of general conditions, and such work, therefore, often assumes great magnitude in the expenditure of money, and requires the most careful planning and negotiations of a financial nature before final arrangements are made and actual work begun.

Usually it is a comparatively simple matter for a rich city to raise the necessary funds for the work by issuing bonds and taking care of the interest and sinking fund charges in the tax-rate. With the railroads it is another matter altogether. Railroads are not able to borrow money by means of a specific bond issue for a purpose which is unproductive of revenue. No one wants to buy such securities. The railroads, therefore, are almost always forced to provide the funds out of revenue derived from the regular business of the railroad. It frequently happens that the expenditure of such large sums is a very serious matter when the regular fixed charges, dividends, and other necessary expenses must be provided for.

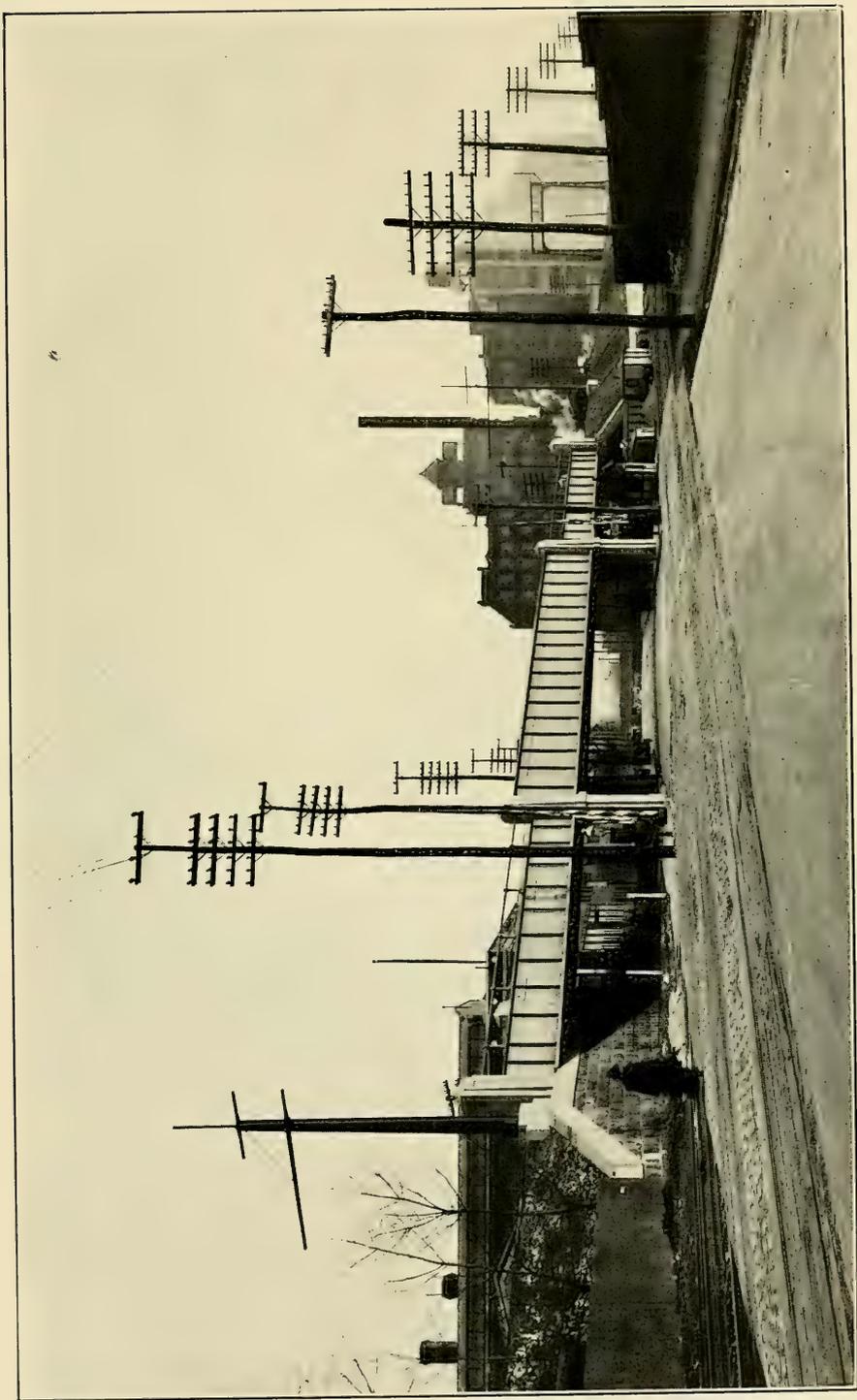
From what has been said it is evident that the rate of the removal of the grade-crossings on any one railroad system can be proceeded with only from time to time as the company can earn sufficient money by means of its regular revenue. Any wholesale expenditure would be disastrous. It is further evident that the public derives important and continuous benefits from the elimination of grade-crossings, while, generally speaking, such elimination means to the railroad company serious increases in its fixed charges for interest on the money expended, serious increases in the cost of maintenance, and, in many cases, serious loss of revenue from cutting of sidings and loss of business. Notwithstanding these facts, railroad companies are generally willing and ready to undertake the work of abolishing grade-crossings, provided the neces-



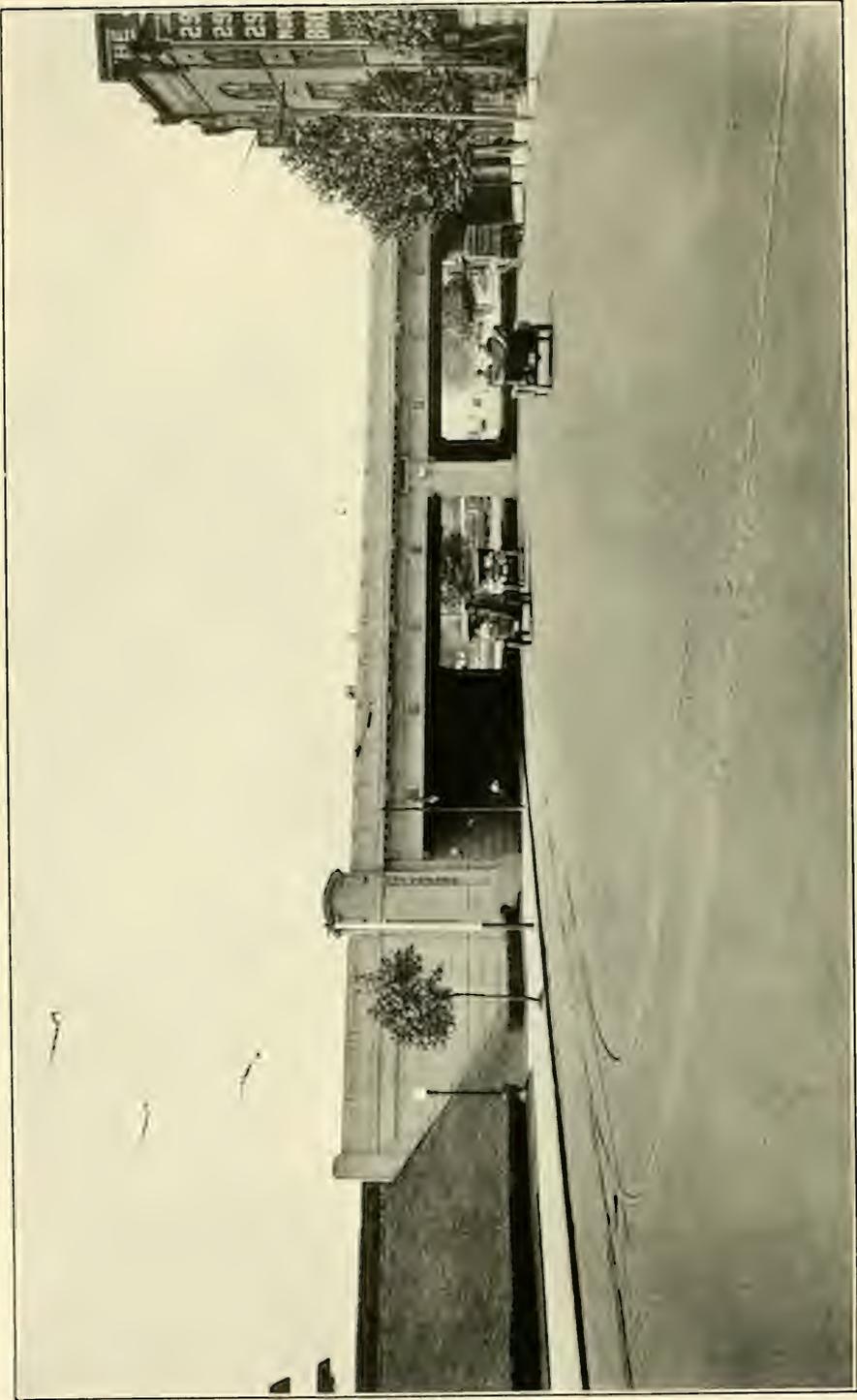
Philadelphia and Reading Railway over Spring Garden Street, Philadelphia, Pa.



Delaware, Lackawanna and Western Railroad over street, Madison, N. J.



Chestnut Hill Branch. Pennsylvania Railroad, over Allegheny Avenue, Philadelphia, Pa.



Pennsylvania Railroad over Broad Street, Philadelphia, Pa., at North Philadelphia Station.

sary funds can be procured and provided the public authorities are willing to share the cost on fair terms.

5. CLASSIFICATION

For the reasons given in the preceding caption, it is evident that the most careful consideration must be given to just where the moneys which both cities and railroads can afford to spend for grade-crossing elimination should be spent. This involves a careful analysis of each crossing, regarding the amount of traffic of all classes, both railroad and street, which passes over it in order to determine its importance, and naturally leads to a plan by which all crossings should be classified. When this is done, it is comparatively a simple matter to pick out the most dangerous and arrange for their elimination. If such a classification be established, say into three classes, arranged in order of their importance, no crossing in the second or third class should receive consideration while a crossing remains in the first class. There is frequently a temptation, which may be caused by influential local interests, to provide for the removal of a crossing of comparatively little importance and leave a very dangerous one unprovided for. The work cannot all be done at once. The most dangerous should receive attention first.

Traffic counts should be made for all crossings, and in the compilation the exact character of the traffic should be noted, as well as the delays caused. A note should always be made defining the character of the railroad traffic. High speed trains are much more dangerous than slow speed freight movements. In many cases the freight movement in a city is entirely of a shifting character and its danger is thus minimized. It may, however, be troublesome and annoying if it blocks traffic on the streets; therefore the necessity for records of this kind.

6. ESTHETIC CHARACTER OF THE CONSTRUCTION

The appearance of the structures erected in grade-crossing elimination in cities is receiving more and more attention, and it is right that it should be so. In many cities of the larger sizes commissions are now in existence whose duty it is to see that the designs of the structures are as pleasing as possible. The engineers of both city and railroad should have this constantly in mind. Unfortunately nothing is harder than to design structures of this class and have

them both economical and esthetic, but because it is difficult it should not be overlooked.

There is no class of bridge structure that is more pleasing to the eye than an arch of masonry, nor more lasting and satisfactory from the standpoint of maintenance, and if sufficient height can be obtained from rail to street, or vice versa, without too much cost, the arch should be used. In any extended piece of crossing elimination involving a number of adjacent crossings it is very difficult to obtain sufficient headroom for an arch without resulting in a practically prohibitive cost, and generally some form of steel or reinforced concrete construction of the plate girder or flat slab type has to be used.

When such construction has to span a wide street or a number of tracks, it becomes necessary to provide a number of intermediate supports in order to design a structure with sufficient strength with a moderate depth. For many years cities would not allow any such intermediate supports except along the curb lines of the streets. If the driveway of the street was wide, this made it necessary to provide a steel girder, or even a truss of such depth as to be decidedly unsightly. Recently a decided movement for the improved appearance of such structures has developed by allowing supports to be placed in the middle of the driveways, as well as along the curb lines. This makes it possible to reduce the depth of the structures so that no part of them is above the top of the rail of the tracks. This provides a safety condition, as far as the railroad is concerned, in removing obstructions which are dangerous to trainmen. The supports in the middle of the driveway are no longer dangerous to vehicular traffic in the streets when one considers that when traffic has to be regulated a policeman is placed in the middle of the street, to keep each line of traffic on its proper side. The case of the Pennsylvania Railroad crossing over Broad Street, Philadelphia, at the North Philadelphia Station, where the supports are in the center of the driveway, is of this kind, and no one would for a moment consider that they were objectionable.

If it becomes necessary to place steel girders over a street, it is much better to arrange the details so as to allow the girders to show, and treat the whole structure architecturally, than to attempt to cover the steel with ornamental work of some kind. A splendid example of this kind of treatment is the Chestnut Hill Branch of the Pennsylvania Railroad crossing Allegheny Avenue, in Philadelphia. The painting of steel girders to match the concrete which

generally forms the masonry support is another decided improvement. The engineer and the architect must work together in all such designs.

There are a few details of the construction of the bridges required either for the railroads or the streets which are important. Sufficient depth must be provided to give a satisfactory floor construction. This must be about four feet. It is necessary to cover the floor of a railroad bridge over a street in a city with solid construction, so as to make it waterproof and prevent drippings onto the street beneath and also to allow standard track construction of ties and ballast to prevent undue noise. It is also advisable to protect the underside of a floor of a bridge of a street over a railroad so as to prevent corrosion of the metal from the fumes of the locomotive. In the State of Pennsylvania the clearance from a street to the underside of a railroad bridge crossing it must be at least fourteen feet. When a street crosses railroad tracks the Public Service Commission is insisting on a clearance of twenty-two feet when it can be possibly obtained, and this is also good railroad practice.

7. TWO TYPICAL EXAMPLES OF WORK IN PHILADELPHIA

Our own city furnishes two interesting cases of grade-crossing elimination which it may be profitable to compare. They are: First, the Subway and Tunnel on Pennsylvania Avenue on the Reading System, and second, the so-called Elevated on Ninth Street and through the Tioga district on the same system.

1st. On the Pennsylvania Avenue Subway seventeen grade-crossings were eliminated, including important ones at Broad Street and at the Spring Garden entrance to Fairmount Park. The work covered a distance of two miles, generally of tracks depressed beneath the surface of the streets in an open subway and a tunnel. Travel was largely diverted during construction to other lines or to adjacent streets. An entirely new system of sewers was necessary, involving a cost of about \$500,000. All yards and other railroad facilities were depressed. The total estimated cost was \$6,000,000, and the actual cost, including all consequential damages, was \$5,500,000. This cost was divided evenly between the city and the railroad company. The work represents a cost of \$2,750,000 per mile of structure. Generally there are four tracks. The time consumed in construction was about five years.

The work was planned in 1894, and the ordinance of councils authorizing its construction was passed on March 17th of that year. At that time the

railroad was in the hands of receivers, and an agreement was made by which the city was to raise the necessary funds by issuing bonds and care for the work of construction and the railroad was to reimburse the city for its share of the cost in regular instalments. The railroad was sold under foreclosure proceedings in 1896, and the new railway company assumed the obligation of the receivers.

2nd. On the Ninth Street Elevated twenty-nine grade-crossings were eliminated, some of them of a very dangerous character. The work covered a distance of 3.7 miles and consisted of elevated tracks carried by masonry walls and earth fill between the streets and steel bridges crossing them. There was also about three-fifths of a mile of elevated steel viaduct over the bed of Ninth Street, allowing the use of the street beneath. All the yards of the railroad were elevated. Travel was maintained at all times during construction by building one half at a time. The estimated cost of the work was \$7,659,740, and the actual cost, including consequential damages, was about \$7,000,000. This represents a cost of \$1,891,900 per mile of structure. Generally there were four tracks elevated. Part of the work was for five tracks. The city and the railroad divided the cost of all construction work and consequential damages necessary to provide equal accommodations to those originally existing. The railroad paid for all betterments. The city issued bonds to pay for its share of the work. The railroad paid its share out of its earnings. All work affecting the operation of the railroad was done under contracts prepared and executed by the railroad after due approval by the city. All work in the streets was contracted for by the city after proper approval by the railroad. The work was done under an ordinance of councils dated October 13, 1906, which authorized the city and the railroad to enter into an agreement. The time consumed in construction was a little over four years.

8. CONCLUSION

There can be no argument against the advisability of the elimination of grade-crossings in cities. Such work removes a condition which is objectionable from every standpoint. They are dangerous to travel of every kind.

Before any crossing or sequence of crossings is eliminated, care should be taken to insure their relative importance compared with others.

The rapidity of such elimination should be determined both by the city and the railroad after careful consideration of their respective financial conditions. The city should consider how much it can properly spend in any

given time, taking into consideration the demands for other public improvements. The railroad should provide for its fixed charges and the growing demand for better service of all kinds. Neither the city nor the railroad is justified in entering into any work of such magnitude as will cripple other necessary demands.

The detail question as to how the crossings are to be eliminated depends upon the conditions of each and every case and should be decided only after the most careful studies. The ruling factors are efficiency, economy, minimum damage to adjacent property and such esthetic consideration as is possible.

The division of cost between the interests involved is a most difficult one. It depends to a certain extent upon the priority of the location of the railroad or the street and possibly on other local considerations. In the majority of cases when there is a similarity of interests a fair beginning for the negotiations for the discussion of cost is upon an equal division between the interests involved.



Topographic Map of the Philadelphia District (U. S. Geological Survey); the 200-foot contour traced in heavy black line, indicating the "fall line" ("Upland terrace"), the line of demarcation between the Coastal Plain and the Piedmont.

THE LIFE FEATURES OF THE COASTAL PLAIN AND THE PIEDMONT

SPENCER TROTTER

Delivered April 9, 1917

I

THE REGION of Old Appalachia is probably one of the most ancient land surfaces on the globe. Unlike many other areas, it appears never to have been wholly submerged, but to have existed at first as a series of detached island masses to the south and east of the great primordial Archean of Labrador. As such it became the nucleus of later successive stages of land-building that ultimately developed into the eastern portion of the North American continent. The weathering of its rock surface supplied the material for future land growth, and we now behold it worn down to its roots—a basal complex of crystalline schist, granite, and gneiss. It is this old land surface that today we call New England and, south of the Hudson Valley, the Piedmont Plateau. The hundred-fathom line marks the edge of the continental platform, and Appalachia may at one time or another have extended to this boundary as an uplifted land surface, but for long periods of time it was submerged and overlaid with sediments. Not until the later Tertiary deposits of sand and gravel had accumulated to a considerable thickness was there an upwarping movement that added a more or less permanent land area along the southeastern border of the continent—the present Atlantic Coastal Plain.

The physical features of these two adjoining land surfaces, the one of ancient archean rocks, the other of the more recent Tertiary sands, are strongly contrasted. At the present time the Coastal Plain of New England is, for the most part, under the sea, granitic rocks forming the rugged coast line of the land. From Cape Cod southward there is an increasingly wider and wider area of coastal plain country until it merges with the Gulf lowland of like age and formation. South of the Hudson the line of demarcation between the Coastal Plain and the Piedmont becomes very apparent. The former presents a generally flat expanse of lowland, gravel, sand, and clay deposits, through which the smaller streams have everywhere cut trenches on their way to join the alluvial reaches of rivers that flow slowly seaward into tidal estuaries.

These estuaries are the upper portions of "drowned" valleys which have been invaded by the sea in a general sinking movement of the Coastal Plain over wide areas. The beginning of this subsidence is a geologically recent event, though a broad belt of coastal plain has already disappeared beneath the bordering sea. Along its western edge the Coastal Plain lies against the old crystalline rock of Appalachia. The first settlers along the lower Delaware noted the contrast between the two regions. They marked the Piedmont as a low rise of land to the north and west—the beginning of a rolling "upland" country. To the tidal mouths of the streams that flowed down from this upland the early settlers gave the name of "creeks," a term proper enough for a tidal inlet, though it has been curiously extended to the upper courses of these streams, that in a rightful sense are not creeks at all, but "brooks." The Piedmont is a plateau of moderate elevation, varying from two hundred to six hundred feet above sea-level, and extending westward to the Blue Ridge. It is traversed in its Middle Atlantic portion by several considerable streams, as the Delaware, Schuylkill, and Susquehanna, which head beyond its western limits and flow through comparatively wide valleys, while the numerous smaller tributaries of these rivers have dissected the plateau into a rolling upland of hill and dale. The line of demarcation between this upland Piedmont country and the Coastal Plain lowland may be traced for a long distance as a more or less conspicuous elevation from the western side of the lower Hudson to Alabama. It is the easternmost limit of the archean gniess and schists of the old Appalachian land, and as such it marks a "fall-line" of rivers from their Piedmont courses on to the Coastal Plain. Above this "fall-line" the streams pursue a more or less rough-and-tumble course, much beset with "rifts" of eroded rock and loose shingle, in marked contrast to their deeper, smooth-flowing reaches on the Coastal Plain alluvium. This geologic feature exerted an interesting influence in the history of settlement, as it marked the upper limit of tide-water navigation in conjunction with water-power facilities from rapids and falls, and it thus became the site of towns, some of which grew into large cities. Trenton, Philadelphia, Baltimore, Washington, Richmond, Petersburg, Raleigh, Augusta, and Macon are located on the "fall-line." In the Philadelphia district this boundary between Coastal Plain and Piedmont is marked by the 200-foot contour (U. S. Topographical Survey Maps). It presents a well-defined rise of land—the "upland terrace," trending along the western edge of the flat lowland expanse of Coastal Plain. From various points it

gives outlooks over this lower country which to most of us are well-known sites—Fox Chase, George's Hill in Fairmount Park, the ridge above Wayne Junction and the Midvale Steel Works, the Baltimore Pike at Primos, Swarthmore College, and Allen's Hill near Wallingford, are some of the more familiar points of overlook. Back of this "upland terrace" the hill and dale scenery of the Piedmont Plateau stretches away to the north and west.

II

This boundary not only separates two strongly contrasted physiographic areas, but likewise forms a dividing line between a more northern and a more southern life, a frontier in the distribution of certain species of animals and plants. As is well known, the continent of North America is primarily divided into two great life regions,—a northern or "boreal" and a southern or "austral,"—each one of which is characterized by certain types of plants and animals, the southern and northern ranges of which are restricted along a more or less narrow intervening territory, the so-called "transition zone," where many of these northerly and southerly species mingle. It is thus a region of overlap, and fully justifies its name. These two contrasted primary areas probably represent, as Merriam* has pointed out, a geographic division of life as the result of temperature conditions, especially in relation to the period of reproductive activity. The division has, however, a much wider significance than the present conditions of temperature would imply, and probably represents a very ancient impress of certain factors that developed at the close of the last glacial period. Along the eastern side of the continent this northern or boreal life element is found to extend some distance to the south along the higher ranges of the Appalachian Mountain system, similar conditions to those prevailing in the north being present as a result of altitude. In like manner many southern species intrude northward along the bottom-lands of river valleys, so that the line of demarcation is everywhere quite irregular. In eastern Pennsylvania a truly boreal condition is found only in isolated patches on the higher portions of the Alleghanies, while a transition type prevails throughout the lower ranges and is the essential feature of the entire Piedmont Plateau. The collective animal life of this territory is known as the Alleghanian fauna and is typically "transition" in its character, while the boreal

* Merriam, C. Hart, M.D.: "The Geographic Distribution of Life in North America." Smithsonian Report, 1891.

animal life of the higher areas is a southward occurrence of the so-called Canadian fauna of the more northern regions. The peculiar interest which attaches itself to the physiographic boundary between the Piedmont and the Coastal Plain in southeastern Pennsylvania is that it marks, in a more or less definite way, a line of demarcation between the Alleghanian type of life and a decidedly southern or austral type of life, a group of species which has received the name of Carolinian fauna. The "upland terrace" or "fall-line" is thus approximately the boundary between a northern and a southern life element.

In the neighborhood of Philadelphia this difference between the northern and southern life features is quite apparent. The Coastal Plain region to the south and east is characterized by a decidedly Carolinian type of fauna, while the upland country to the north and west of the city is occupied mainly, as before mentioned, by Alleghanian or transition-zone species. The distribution of certain birds during the breeding season is a good index of this difference in the two areas. The Worm-eating Warbler (*Helmitheros vermivorus*), a typical Carolinian species, is much more abundant in the woodlands of the southern section of the Philadelphia district than it is in the northern portion, occurring only sparingly in the upland country, and there confined to the timber along the bottom lands of the streams that flow down among the hills. This species may be said to reach the northward range of its distribution on the Atlantic slope along the lower Delaware Valley, and is mainly confined to the western side of the river, being of rare occurrence in southern New Jersey. It is likewise found during the breeding season in the lower valleys of the Hudson and the Connecticut rivers, but not in the intervening higher land, a fact indicating that certain physical conditions are present in these two river bottoms similar to those prevailing in the lower Delaware and southward. Like features of distribution are also true of two other species of warbler—the Blue-winged Yellow Warbler (*Vermivora pinus*) and the Kentucky Warbler (*Oporornis formosus*), though these birds have penetrated more generally into the woodlands for some distance beyond the Piedmont border. The Carolina Wren (*Thryothorus ludovicianus*), the Carolina Chickadee (*Penthestes carolinensis*), and the Tufted Titmouse (*Baeolophus bicolor*) are other species much more abundant in the Coastal Plain region than in the hill country to the northeast of the city. It must be borne in mind that this border line from the Susquehanna southward largely loses its significance as a faunal boundary from the fact that an increasing southern latitude exerts more and more of an influence,

bringing a wider and wider area of the Piedmont within the realm of the Carolinian fauna. This accounts for the greater abundance of some of the above-mentioned species among the hills of the Piedmont in southern Chester and Lancaster counties and the lower Susquehanna watershed.

Certain other birds are typical of this Carolinian region about Philadelphia—the Yellow-breasted Chat (*Icteria virens*), the Acadian Flycatcher (*Empidonax virensens*), the Cardinal Grosbeak (*Cardinalis cardinalis*), the Barn Owl (*Aluco pratincola*), and the Turkey Buzzard (*Cathartes aura*) are all increasingly more abundant in the south. It is a noteworthy fact that some of the above-mentioned species, as the Cardinal, the Carolina Wren, the Carolina Chickadee, and the Tufted Titmouse, are resident birds throughout the year, wintering along this northern border of the Carolinian fauna in the region about Philadelphia. In former years the Mockingbird (*Mimus polyglottos*) appears to have been much more numerous than at the present time and to have wintered in this vicinity. Among mammals the gray fox and the opossum, characteristic austral species not ranging to any extent beyond the limits of the Carolinian fauna, are much more numerous on the Coastal Plain lowland, the former being rarely found in the hill country. The distribution of certain reptiles in like manner indicates this region of the lower Delaware Valley to be more or less distinctly of the nature of a faunal barrier. The common Box Turtle (*Terrepenne carolina*) that we meet with so frequently in our woodlands is a characteristic austral type, and the same may be said of the Ground Lizard (*Leiolopisma laterale*) and the little, active Swift Lizard (*Cnemidophorus*). The celebrated "Diamond Back" Terrapin (*Malaclemmys*) and the Red-bellied Terrapin (*Pseudemys*) do not range north of the Carolinian fauna. Muhlenberg's Tortoise (*Clemmys*) is curiously local in east Pennsylvania and southern New Jersey. Among snakes the Corn and the Chain Snakes (*Lampropeltis*), the Water-Snake (*Natrix sipedon erythrogaster*), and the Pine Snake (*Pituophis*) are limited northward in the same way, while the Copperhead (*Ancistrodon contortrix*) is rare north of this faunal boundary. In the same way the little Green Snake (*Ophedryx aestivus*) appears to be more or less limited in its northward distribution.

III

The question of the distribution of these Carolinian types turns on the factors that are involved in thus limiting their northward ranges. Tempera-

ture can scarcely be regarded as a controlling factor, although Merriam bases his scheme of faunal zones on this as the main issue. It seems unlikely that any such differences in temperature could exist on either side of this faunal boundary as to affect vitally the reproductive functions of closely allied species of birds or of reptiles. The Kentucky Warbler, for example, belongs in the same genus (*Oporornis*) with the Mourning Warbler and the Connecticut Warbler. All three are birds of very similar habits and life relations, and yet the two latter breed entirely beyond the limits of the former species. The same is true of the Golden-winged Warbler and the Blue-winged Yellow Warbler, of the two species of Chickadee, and of the Acadian Flycatcher and its near relations the Least and Alder Flycatchers. Nor is it conceivable that any such differences in temperature, prevailing over the upland and lowland, exist as to form a reproductive barrier. The "effective temperatures" adduced by Merriam are averages made to fit the facts of distribution. The causes must be looked for elsewhere.

The most significant feature in the distribution of the Carolinian fauna in the lower Delaware Valley is its relation to the Coastal Plain. As we have seen, this Coastal Plain in southeast Pennsylvania and southern New Jersey is a narrowing northward extension of a wide southern territory which is characteristically austral in its forms of plants and animals. The relation between a land and its life is unquestionably a relation established by geologic conditions rather than by any direct climatic influence; it is in the nature of a historic sequence dependent upon an ancient underlying cause—in this instance the addition of a coastal continental margin of land which began some time during the Tertiary. By a slow process of uplift land was added along the eastern border of Old Appalachia, at first most likely as a fringe of bars and beaches between which and the main land salt lagoons with their characteristic vegetation of sedge forms appeared. Further uplift would gradually convert lagoons into drier areas of sand and clay, and new lagoon conditions would form to seaward. At a later period a considerable strip of this Tertiary uplift suffered submergence, a state of affairs probably still going on as already noted. At the southern end of Appalachia, this Atlantic Coastal Plain merges with the great Gulf lowland—an uplift of the Mississippi embayment of early Tertiary time which embraces the whole lower coastal of Texas and the Gulf States to the present site of the Ohio confluence. The time involved in the gradual emergence of this alluvial sand and clay, which represents the waste of an enor-

mous area of the old continent (the Mississippi-Missouri-Ohio drainage basins) was probably not less than two million years, and the rivers on the eastern slope of Appalachia were wearing down their basins at the same time and adding to the formation of the Atlantic Coastal Plain. Professor Edward W. Berry has shown that during the Lower Eocene time the shores of the "Mississippi Gulf" were covered by a luxuriant vegetation of tropical forms allied to those of existing families, and even genera, in other parts of the world.*

With the gradual lowering of the temperature, due to secular changes in climate and the appearance of glacial conditions in the north, a warm temperate flora must have gradually taken the place of the earlier tropical types, spreading over the lands of recently emerged lagoon bottoms. It is with this later forest that our interest chiefly is concerned.

The northern hardwood forest is more or less typical of the so-called "transition zone" of Merriam, and is the characteristic woodland of Appalachia, extending over New England, the greater portion of the Alleghany Plateau, and the Piedmont of the middle Atlantic slope. It probably originated in post-Pleistocene time, after the recession of the glacial ice and under existing climatic conditions. Among conifers the white pine and the hemlock cover wide areas, the former prevailing especially in sandy soils, while among the chief deciduous types are the beech, the birches, several species of maple, the elms, and the linden or basswood. To the north this forest gradually gives way to the great boreal coniferous zone of spruce, fir, and tamarack, mingled with birches and aspens. From the lower Delaware southward, the Piedmont and the contiguous border of the Coastal Plain are covered by a woodland of very different character. This forest reaches its maximum development in the central region west of the Alleghanies and extends in a narrow belt around the southern end of the highland country. It is essentially a forest of rich and deep alluvial soils and is remarkable for the great variety of trees. Among these are many different kinds of oaks, several species of hickory, the buckeyes and the tulip tree, besides numerous other forms, as the chestnut, ash, and a variety of underwoods. Along its southern and eastern borders these tree types are mingled with others of decidedly Coastal Plain distribution, notably the liquidambar or sweet-gum and the black gums or tupelos. On Sargent's map this woodland appears as the Interior Hardwood Forest. The wide stretches of Tertiary sands that form the seaward border of the Atlantic and Gulf coastal

* Berry, Edw. W.: "The Mississippi Gulf Three Million Years Ago." *Scientific Monthly*, 1917, 4, 274.

are covered for the most part by a characteristic growth of pines, comprising a number of different species. In the low-lying, wet districts, along bays and water courses, the white cedar forms characteristic swampy jungles, and from the Chesapeake southward the bald cypress is a conspicuous tree of the flood lands.

What particularly interests us in this distribution of forest trees is the fact that this more southern type of woodland prevails in the district immediately south of Philadelphia, *i. e.*, in the Coastal Plain area, while on the uplands north of the city it is far less conspicuous. This is notably the case with the Sweet-Gum (*Liquidambar*), a tree which in this region is on its northern limit and is more or less restricted to the Coastal Plain. The same may be said to be true of the Willow Oak (*Quercus phellos*), of the Pepper-bush (*Clethra*), and of the Swamp Magnolia or Bay (*Magnolia virginiana*). It is with this particular type of woodland that the Carolinian fauna is associated. In the Choptank Swamp, which extends to the southern border of Delaware, certain birds of decidedly austral distribution occur regularly during the breeding season, and this locality is the northeastern limit of their range. Among these truly Gulf coastal species are the Yellow-throated, Prothonotary, and Caerulean Warblers, the Gnatcatcher, the Brown-headed Nuthatch, Louisiana Water-thrush, Summer Tanager, Blue Grosbeak, and Red-bellied Woodpecker. These are all birds of the southern and the interior forests. The southern portion of New Jersey is interesting as being the northern extension of the Tertiary sands of the Coastal Plain and is covered by a characteristic pine woodland quite similar in aspect to that which prevails throughout the south. These "pine barrens" are interspersed with the "cedar swamps" already mentioned, and the whole region harbors certain characteristic species of birds, one of which is curiously related to a scrub oak and pine woodland. This is the little Prairie Warbler (*Dendroica discolor*) that is everywhere distributed, more or less southerly, in relation to such areas. It is almost entirely absent during the breeding season on the western side of the Delaware, where the alluvial type of woodland prevails. Conversely, the Worm-eating Warbler is never found in the pine barren district on the New Jersey side. This is an excellent illustration of distribution in relation to *habitat*.

It is this question of "habitat" on which much of the problems of the distribution of animals in general depends. Faunas may thus be considered from two standpoints—*geographic* and *ecologic*. In any given area of varied physiography and topography the animal life will be distributed in rela-

tion to the variety of surface conditions—forest, grassland, desert and scrub, swamp, jungle, and river shore. Each one of these fundamentally vegetational differences constitutes a “habitat” for some group of creatures. The fauna of a region is thus the sum of as many local or habitat faunas as exist within the region itself. The regional fauna is, in the main, a geographic problem; the local, habitat fauna is a problem in ecology. This relationship to particular tracts of country on the part of any species of animal is a part of the species’ history and in most cases is of considerable antiquity. Both of the above-mentioned birds belong to the Carolinian fauna, so far as their regional association is concerned, but the Prairie Warbler is a “pine barren” type, while the Worm-eating Warbler’s ecologic affinities are with the hardwood growth of the interior forest.

It must be already quite clear that in the Philadelphia district we are surrounded by the remnant of this great southern interior hardwood forest on its northeastern fringe, and that, near at hand, just across the Delaware in New Jersey, are the “pines”—the northern frontier of that vast pine woodland of the South Atlantic Coastal Plain. In colonial days a line run by the English surveyors, Mason and Dixon, arbitrarily fixed a boundary that in after-years made a “North” and a “South.” The real physical and biological “South,” however, as we now know it, reaches to the fall-line of the lower Delaware, and the city of Philadelphia touches the edge of “Dixie-land.” One with an eye for the countryside realizes this—the clear whistle of the Cardinal and the loud chant of the Carolina wren betoken it, as well does the lazily soaring turkey buzzard, the strange barn-owl, the casual opossum, the groves of sweet-gum trees, and other no less characteristic features. To be sure these sometimes are seen beyond the fall-line, but never so abundantly as on the Coastal Plain to the south.

IV

The existing forests of eastern North America probably date back to the Miocene period. At that time a mild climate, most probably a warm temperate climate, enveloped the circumpolar area, and a luxuriant vegetation flourished to within at least twelve degrees of the north pole. Professor Heer and other students of paleobotany have found in the Tertiary deposits of Greenland and Spitzbergen a large number of fossil remains of plants which are closely allied to forms now living in eastern Asia and eastern North America. Among these are a number of forest trees, identical in some instances with existing species, as the liquidambar, the tulip tree (*Liriodendron*), the sassafras and magnolia.

These forms are now quite restricted to the above-mentioned regions. Remains of more widely distributed types, as the plane tree (*Platanus*), the basswood (*Tilia*), the persimmon (*Diospyrus*), besides several varieties of birch (*Betula*), aspens (*Populus*), oaks (*Quercus*), and beeches (*Fagus*), have also been discovered in Greenland, indicating the existence of a rich and varied woodland not unlike that of the modern temperate zone forests of Eurasia and North America.*

As Professor Berry has pointed out, there is evidence that a rich tropical vegetation flourished along the shores of the old Mississippi embayment three million years ago, and it is probable that this circumpolar warm temperate type was developed during the same time and continued throughout the succeeding Miocene and Pliocene periods. Secular changes of climate occurred, as we know, several times throughout the Pleistocene, covering vast periods of time, and marked by four distinct glacial epochs. It is not unlikely that the present conditions of climate and vegetation in the northern hemisphere may be of inter-glacial character, similar in many respects to the inter-glacial epochs of the Pleistocene. The lowering of temperature at the outset of glaciation undoubtedly had a marked effect on this circumpolar Tertiary forest, blotting it out entirely in the more northern part of the area, while it still continued to flourish farther to the south, the hardwoods acquiring a deciduous habit with the rhythmic recurrences of seasonal cold that marks our present year. Dr. John Harshberger, in a most suggestive paper on the "Origin of our Vernal Flora,"† has shown that in all probability the present rhythm of vegetational function in northern lands had its origin in the conditions of seasonal temperature during the last glacial period.

Throughout the lapse of the Tertiary the slow upwarp of the continental platform along the eastern and southern Atlantic border was gradually adding new land, the sands and clays of the marginal sea-floor becoming a Coastal Plain land surface. A forest would find favorable conditions on this new land and would spread out from the lower southern portion of the Piedmont, the various types developing in situations determined largely by the nature of soils. Pines and scrub oaks would spring up and cover sand tracts, as we have seen; other forms would find suitable rootage in the deep alluvial soils of stream bottoms and the side slopes of mature valleys both on the Piedmont and the

* "The Relations of North American to Northeast Asian and Tertiary Vegetation." Article V in *Darwiniana*, by Asa Gray.

† "Science," [N. S.] 1895, 1, 92.

contiguous Coastal Plain. Thus the sweet-gum (*Liquidambar*) is peculiarly a tree of stiff clay lands and the same is true of other species. The boreal coniferous forest of spruce, fir, and larch and their associate hardwoods—birch, aspen and willow, long enured to low, moist temperatures—would survive as a northern forest belt, while all the old Miocene warm temperate types would survive only to the south of this, and many found the conditions best suited to their development on the border land of the Piedmont and the Coastal Plain. How came the animal life of this forest?

A brief survey of the bird fauna of eastern North America and its distribution during the breeding season will perhaps throw some light on the history of animal life in this forest region. There is a distinct northern element consisting of types more or less wide-spread in both Eurasia and North America and associated apparently with the spread of coniferous boreal woodland. Of these are certain finches, as the Purple Finch (*Carpodacus*), the Pine Grosbeak (*Pinicola*), the Evening Grosbeak (*Hesperiphona*), an American form closely related to the Old World Hawfinch, and the Crossbills (*Loxia*). Likewise the Creepers (*Certhia*), the Nuthatches (*Sitta*), the Titmice (*Penthestes*), and the Kinglets (*Regulus*), the corvine birds, as the Crows and Jays, the Wax-wings (*Bombycilla*), the Northern Shrike or "Butcher-bird" (*Lanius*), and certain other species belong essentially to Palearctic or northern Old World types. Another element of our eastern woodland bird life was derived from the dry plateau region of Mexico and southwestern North America, according to Dr. J. A. Allen.* Our Bluebird (*Sialia*), the Thrasher (*Toxostoma*), the Chewink (*Pipilo*), and the Wild Turkey (*Meleagris*) are wanderers from this center of development, the majority of the closely allied species being still found in the aforesaid region. The rest of our land bird types are either invaders from the tropics or are indigenous to this eastern region itself. The invasion of tropical forms, like the orioles, the tanagers, the cardinal, the rose-breasted grosbeak and blue grosbeak, the indigo-bird, and certain warblers was probably coincident with the widening Gulf and South Atlantic border of the continent, which became the Coastal Plain. These early established themselves as breeders throughout this woodland area. The late Arthur Irwin Brown has shown very conclusively† that this great southern forest of the Atlantic and Gulf Coastal Plain was a post-glacial center of dispersal of reptiles—an "Ocmulgian" center,

* "The Auk," 1893, 10, 9.

† Proceedings of the Academy of Natural Sciences of Philadelphia, 1904, 56, 464.

as he termed it. The significance of faunas, or the regional distribution of groups of species, appears to be a phase in the gradual spread of animal life which accompanied the development of certain types of vegetation. Thus the Carolinian fauna is clearly related to the Coastal Plain and the contiguous hillslopes of the southern Piedmont. The entire region is one of diverse habitat elements, as already pointed out. That certain of its animal types tend to spread beyond its generally recognized borders is seen in the breeding ranges of such decidedly austral birds as the wood-thrush, the chewink, the field sparrow, the indigo-bird, the rose-breasted grosbeak, the whippoorwill, the dove, the scarlet tanager, and the orchard and Baltimore orioles which have extended well into the Piedmont region, including its New England portion. This group of species is typical of the Alleghanian or transition zone fauna. Furthermore, there is a marked movement of certain Carolinian species into the cleared areas of the upland region. "A fauna," as I have elsewhere remarked,* "is an expression of the temporary adjustment of any group of living beings to given conditions of environment. . . . In the sum of its conditioning factors character of vegetation is probably the most important determining influence. . . . All species tend to spread, as their ancestral types have spread wherever suitable habitats are accessible to them."

In bringing this paper to an end I feel constrained to conclude with words which I have elsewhere used in an endeavor to portray the relations of a fauna to the geologic history of the land, especially with reference to the formative influences of the last glacial period: "Throughout an immense lapse of time, time that must be reckoned in hundreds of thousands of years, during which the great Keewatin and Laurentide glaciers pushed their ice sheets beyond the present site of the Great Lakes and the Mohawk Valley, forcing southward the animal and plant life into an area of high biotic tension, a wide-spread change in types must have taken place. The most primitive forms have undoubtedly disappeared. . . . It was a period of profound environmental moulding, intensified by the effect of the glaciers on the land and its life. From our limited point of view the array of species and varieties which we see today seem peculiarly stable in their features and their adaptations. But the dynamic influences of environment are ceaseless if inconspicuous. Species and faunas alike are but passing phases in the vast cosmic processes of a continent's history."

* "The Relations of Genera to Faunal Areas," Trotter. "The Auk," 1909, 26, 221.

MENDEL AND HIS LAW

SAMUEL CHRISTIAN SCHMUCKER

Delivered November 14, 1916

ON THE railway which leads from Vienna to Prague, and a little less than a hundred miles from Vienna, is the very ancient city of Brünn. Today it is busy with the spindles of the mills which make it the great city of the woolen industry in Austria and the chief manufacturing center of that country. The various wars of Europe have swept over it and swung it from side to side. When the revolt of the Carbonari broke out in Italy and the Italian revolutionary poet, Silvio Pellico, was arrested for his part in the revolt, he was taken to Brünn. In the subterranean chambers of the prison that rests upon the Spielberg, to one side of the city, Pellico passed the years made so famous in literature by his pathetic story. The first year of Pellico's imprisonment, the year 1822, saw the birth of a peasant boy in the neighborhood of Brünn. Educated for the priesthood, he became a monk in the monastery in this beautiful city between the rivers, and here did a piece of work for which he has since been famed throughout the scientific world.

The world can hold only one big idea at a time, and when Gregor Johann Mendel (the first name, "shepherd," was assumed when he entered the Augustinian order) arrived at his conclusions, the fame of Darwin's theory and his epoch-making work were stirring the scientific world. The battle over the species question was so bitter and so vigorous that no one seems to have had time to notice the Austrian monk counting out his peas in the little cloister of his garden. The world was not yet ready for Mendel's law of heredity, and it lay buried until the year 1900. By this time all the biologic world was studying the problems of inheritance, and three different workers, all acting independently, came separately to a discovery of the obscure publication of this modest monk. Hugo De Vries, the Dutch botanist of the University of Amsterdam, working over the primroses which had spontaneously sprung up in the University botanical garden, became deeply interested in the study of inheritance; his scholarly search for all sorts of published matter bearing on the question led him to the archives of the Society of Naturalists in Brünn. Looking over the back numbers of this publication, he found Men-

del's paper, published in 1866. De Vries at once recognized the importance of the paper, and made known to the world the result of the work of the modest Abbot of Brünn, who had died eighteen years before.

Mendel, in the quiet little cloister garden of the monastery of Brünn, began work with common peas, work that was so patiently continued and so carefully done that the results he obtained gave him a fundamental law which in time to come will probably stand with students of heredity as Kepler's laws stand with astronomers. The work required just such careful, patient, long-continued effort as the monk could easily make. Certainly it did not interfere with his duties enough to prevent his becoming in later life the abbot of the monastery. Mendel had studied botany under Kolreuter, and to him he naturally turned with the result of his discovery. For some unforeseen reason this then famous botanist apparently paid no attention to his communication, and the world, which should have known, was left ignorant of the important discovery. Instead, Mendel read his paper before the little Society of Naturalists in his home town. The report of it occupies forty-four pages of the volume of Proceedings printed in 1866. Mendel attacked the problem of crossing plants from a side which had not yet been touched.

The peculiarity of his process consisted in the fact that he began by crossing plants which varied only in one striking particular, and then paid attention only to the effect of the crossing upon that particular quality. For the experiment which he wished to make it was necessary that he should have a plant that, in the first place, would breed pure, that is, produce only its own like. Second, it must fertilize itself successfully and yet be able to be cross-fertilized by hand, and in the third place, its hybrids must be fertile, which is not often the case. He found that garden peas answered all these qualifications better than anything else he could find. Accordingly, he sent to dealers in garden seeds and gathered a considerable number of varieties of peas. He bred each of these long enough to see which of them could absolutely hand to their offspring qualities always resembling those of the parents. From these he selected the peas he wanted for his purpose. One of the striking differences among his peas lay in the shape of the pea itself when it was ripe in the pod. Some peas were always plump and round, others, no matter how long they were allowed to mature, were always wrinkled. Each of these always handed its quality in this respect to all its offspring. The round pea, planted, grew up into a bush on which every pea was round. The wrinkled pea, on the other

hand, always produced wrinkled peas. It was Mendel's problem to cross these peas. Opening up a blossom before it was ready to bloom, Mendel cut the unripe stamens out of the flower, thus removing the fertilizing element, placed upon the pistil of these flowers pollen from a pea blossom of the other kind, and protected the flower from accidental cross-pollination by insects. He found it made no difference whether he carried pollen from a plant that bore wrinkled peas to the pistil of a plant bearing round peas or made the reverse cross. The result was always the same. The peas were always round. None of them showed the faintest sign of their wrinkled parent. They looked exactly as if both parents had sprung from rounded seeds. The interesting fact turned up, however, that when he planted these seeds of double parentage, they behaved very differently. The vines growing from them produced vines bearing chiefly round peas. A small portion of them, however, came out wrinkled. From this it was evident to Mendel that these hybrid yellow peas, which had one round ancestor and one wrinkled ancestor, could carry, under their seeming smoothness, the power of sometimes reproducing their wrinkled ancestor. Now Mendel began to cross smooth and wrinkled peas and to replant every pea produced by them, keeping an accurate record of the exact number of and pedigree of each sort of seed produced. When he did this, he found that the round and wrinkled peas were always produced in practically the same proportion, that is, of three to one. One can realize how carefully this work was done when we find that in studying the form of these seeds his record for round and wrinkled shows that he had 5474 round peas to 1850 wrinkled peas. This is in the ratio of 2.96 to 1. A little later another experiment with yellow and with green peas gave him 6022 yellow peas to 2001 green. This is in the ratio of 3.01 to 1. It becomes evident here that the law, to which accident naturally will make exceptions, is that these forms will be produced in the ratio of three to one. Accordingly, whenever he crossed round and wrinkled peas, the product in the first generation always consisted entirely of round peas, but these peas replanted produced in the next generation peas three-fourths of which were round and one-fourth wrinkled. These results were repeated so often that there could be no possibility that this figure was a mere accident.

Even this was not the end. As has been mentioned, this second generation had three times as many round as wrinkled. Mendel soon found that not all these three round peas were alike. When planted again, self-fertilized, one-

third of the round seeds produced always round peas, while the other two-thirds produced round and wrinkled in the proportion of three to one. The wrinkled seeds that had come in the second generation always produced only wrinkled seeds. Here comes then the interesting deduction. If two parent peas are one round and one wrinkled, their children will all be round. Their grandchildren will be three round to every one wrinkled. Their great-grandchildren will be disposed as follows: The children of one of the round will all be round and will continue in later generations to produce only round peas. Their blood is as purely round as that of their great-grandfather and every trace of their wrinkled grandmother has entirely disappeared. Similarly, the wrinkled grandchildren will produce only wrinkled through generation after generation. In other words, their blood is as wrinkled as that of their wrinkled grandmother and no trace of their round grandfather remains. On the other hand, two of the round grandchildren have in them both the round blood of their round grandfather and the wrinkled blood of their wrinkled grandmother. Each of them will produce offspring of both kinds in proportion of three to one, and of the three, one will be pure and the other two hybrid. If this seems confusing, the following diagram will probably help to make it clear, and the passage should be re-read until the order underlying it is evident, for this is too important to leave unmastered.

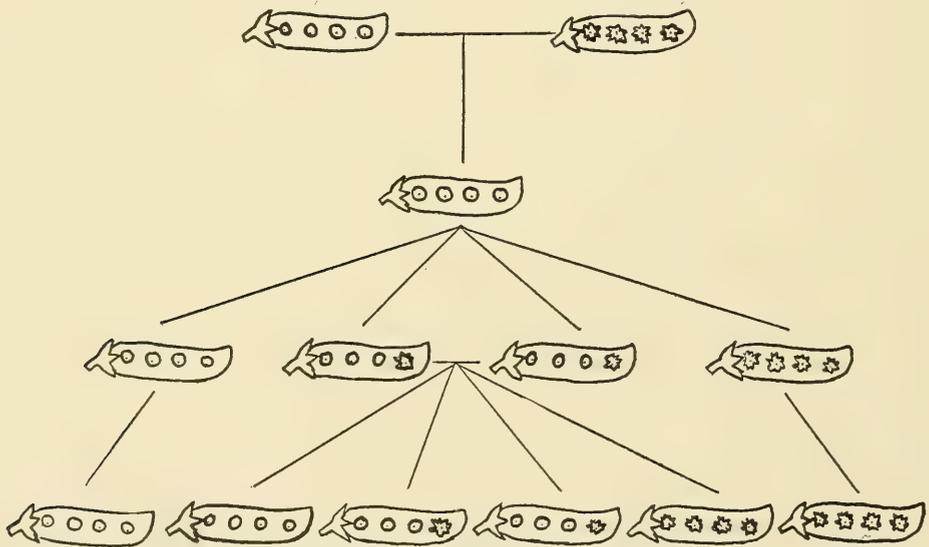


Illustration of Mendel's law.

It is quite evident then that roundness and wrinkledness are very different in their behavior in peas. No one can tell looking at a round pea whether it will always produce round peas. It may be pure bred and may always do so. On the other hand, beneath the roundness there may lie concealed the power inherited from a wrinkled ancestor of producing wrinkled offspring. No wrinkled pea, self-fertilized, however, can produce round offspring. If a pea is wrinkled, its blood in this respect is pure and its descendants will always be pure unless crossed with round peas. Roundness, then, in peas may conceal wrinkledness but wrinkledness cannot conceal roundness. Mendel expressed this by saying that roundness is dominant while wrinkledness is recessive.

Mendel found that when he planted yellow seeds, he might get only yellow or he might get some yellow and some green seeds, but when he planted green seeds, he always got only green. It is evident here that yellowness in peas, like roundness, is dominant, while greenness, like the wrinkled condition, is recessive. Accordingly, when yellow and green peas are crossed, the first hybrid generation is always yellow, but the second hybrid generation is three yellow to every one green. Of these three yellow, one is pure yellow and two are hybrids, producing both yellow and green descendants in the ratio of three to one. Next he tried crossing peas with brown seed coats with others that had white. He found the brown color dominant and the white recessive and that later generations were produced in just the same proportions as had taken place when round and wrinkled or yellow and green seeds were crossed.

Some peas have inflated pods; in others the pods get constricted between each pea and the next. Mendel found on crossing these that the swollen pods were dominant over the constricted, the third generation consisting of three swollen to one constricted. He found two other peas that differed in the color of their unripe pods. Some peas when unripe have green pods, while others have pods which are yellow almost from the first. Here coloring was entirely reversed from what he had found it in earlier experiments. In pods, the green color is dominant over the yellow, and in each generation, after a cross, the proportion is as three to one. Still another pair of qualities in peas were contrasted by Mendel. Some pea-vines bear their blossoms in the axils of the leaves, while others bear them on the tips of the stems. Mendel found that in this respect the axillary condition was dominant over the terminal and no one could tell, looking at an axillary bush, whether the peas on it would spring into more plants with axillary blossoms or whether they would come terminal, but the peas on a

terminal bush, unless crossed, that is, unless fertilized with those of another kind, always come terminal.

One more series of experiments gave him another characteristic in which his peas followed the now well-established law. When he crossed pole peas with dwarf peas, the resultants were always tall, never dwarf, but in the succeeding generation they came in both kinds, there being three tall plants to one dwarf.

Accordingly, in peas, round is dominant and wrinkled recessive: yellowness of seed is dominant over greenness; green seed coats are dominant over brown; swollen seed pods are dominant over constricted; pods green when unripe are dominant over pods yellow when unripe; the axillary position of flowers is dominant over the terminal, and tallness of stalk is dominant while dwarfness is recessive.

The next step taken by Mendel was to find what would happen when he crossed plants which differed in two of the above-mentioned particulars. Accordingly, he took a yellow round pea and crossed it with a green wrinkled pea. As the reader will expect, all the seeds in the next generation were round and yellow. In the second hybrid generation, however, he got

315	seeds, round and yellow	(9)
101	“ wrinkled and yellow	(3)
108	“ round and green	(3)
32	“ wrinkled and green	(1)

A little inspection will show that these numbers are very close to the proportion of 9, 3, 3, and 1. At first it is difficult to see the law underlying this, though the simplicity of the numbers arouses suspicion of a law, but if we look at one quality, one at a time, we will find that there are twelve round peas to four wrinkled, which is as three to one, and there are twelve yellow peas to four green, which again is as three to one. In other words, whether we deal with one pair of qualities at a time or with two pairs, each pair behaves as if it was alone.

He now attempted crossing seeds which differed in three of these striking aspects, and while he found that the result grew apparently more complicated, in reality it was just as simple, and each pair of qualities was behaving as if it were alone, entirely unaffected by the presence of the other qualities.

Mendel's great contributions to our ideas of heredity are: First, plants are mosaics of unit characters, each of which can be inherited independently of

any other. Second, on crossing individuals that differed in a pair of unit characters, the first hybrid generation will show only the dominant member of the pair. The next generation will furnish three dominant, one of which is pure and the other two hybrid, while there will be only one recessive.

At this time little was intimately known of the nature of the reproductive process in plants and animals, but there was enough in what Mendel had done to make him feel that in the fertilizing cells, in ovule and pollen, must lie the secret of the behavior of the individuals which spring from them.

Fourteen years later another paper of Mendel's, in the same obscure journal, tried to solve some difficulties that appeared when St. John's wort plants were crossed, but these hybrids are so complicated that Mendel's second paper lacks the clearness and convincing character of his first masterly composition.

Mendel's law is so entirely the result of painstaking observation that there is no possible question as to its truth concerning a very large number of animal traits. But while it is perfectly clear that the facts are as Mendel states them, there was nothing in his researches to indicate why they are true. He made a few surmises, which in some respects were rather happy guesses, but concerning which neither he nor any one else at the time could have any real certainty.

Not until Weismann made his famous researches was it possible to see any structural reason in the egg itself why Mendel's law should be true. Now it is not hard to see that we are very much closer at least to a structural explanation of the facts expressed in Mendel's law.

There are various avenues by which the scientist has reached his development. Some of our greatest biologists are the product of travel. Darwin's voyage on the "Beagle" was undoubtedly the determining factor in his life. Alfred Russell Wallace did all his best work traveling in South America or in the Malay region. Mendel and De Vries did their great work in the garden. Careful planting and watching and recording made the basis of their training. As a science grows more complicated, as its general truths become well known and investigation becomes the work of the specialist, the laboratory student comes to the front. It was training such as this that gave to the scientific world the thoughtful, painstaking scholarship of August Weismann. This patient worker was born in 1834 at Frankfort-on-the-Main. His life is singularly free from all the ordinary chances and mischances which make up the biography of most men whose lives attract attention. Weismann's career is

singularly uneventful, when looked at from this standpoint. Like many other scientists, his approach was through the study of medicine. He got his training and his medical degree at Göttingen. After practising medicine for a little while he went for further study to Vienna for a year, for another year to Italy, and finally to Paris. Then comes a short interval of medical practice, but his scholarly tastes drive him once more to the laboratory and he goes to Giessen to study under Leuckart. Now instead of returning to the practice of medicine, he goes to the University of Freiburg, in 1866. Beginning there at the bottom in the department of zoölogy, he passes through all the grades of teaching until he reaches the honor of the full professorship. This chair of zoölogy he held up to the time of his death in 1914. His preceptor, Leuckart, had been a famous student of parasitism, and it was perhaps this which led Weismann to the study of certain members of the fly family which are parasitic on or in animals or are in other ways troublesome to man. This led to the study of the life history of these insects, which involved careful and very accurate work under the microscope.

In order that those unaccustomed to the nature of this instrument should have some idea of what is meant by microscopic work it may not be amiss to describe some of the refinements of practice which have developed within Weismann's working years and in the use of which he was most assiduous. Work with the microscope does not mean simply looking at things under the microscope. Some of the most difficult parts of the work must be done before the object can be placed under the glass for examination. The preparation of objects for the microscope has more refinements than the observation of the material after it is once prepared. In the earlier days of biologic study, not over fifty years ago, it was considered quite sufficient for most purposes that the animal should have been killed by any method which brought about its death in decent and seemly fashion. An animal killed by chloroform and then preserved in alcohol was considered perfectly good material for microscopic work. Such a preparation served entirely for all ordinary dissection. When it came to the study, not of the number and size of the cells, but of their internal structure, it became gradually more and more clear that the cells of animals killed in such fashion do not bear in death even a remote resemblance in internal structure to that which had been theirs in life. It was clear that there were very profound changes within the cell on and after death. It became essential, then, that tissues must be brought quickly from life to death and not

only promptly killed but arrested in their processes, so that the condition in which they were caught remained for examination no matter how long this examination might be deferred. Hence arose many "killing and fixing" fluids. Minute animals in water could be suddenly doused with such fluids, with the result that life ceased instantaneously and the tissues became fixed in conditions so complicated and so easily got by repetition of the process, that it seemed probable that these were the conditions during life.

The materials of which cells are made are so transparent that, on looking through the cells, it is very difficult to discriminate one ingredient from another. Accordingly, there has arisen a process of staining to make the different components of the cell evident, which has added much to the accuracy of microscopic work. The principle of this staining can be easily understood if we imagine we have in hand a piece of white woven goods, whose threads are known to be made of mixed cotton, silk, and wool, and the proportion of whose materials we desire to ascertain. It will not be difficult to find a dye which will color the silk with a fixed and permanent color, but which will readily wash out of cotton and wool. Supposing this dye to be red in color. By dipping the cloth into such dye, allowing it to remain until the color has penetrated the fibers, and then persistently washing it, the silk threads will remain red while the wool and cotton will be white as before. Now let us find a blue dye, which is a fixed color for cotton, but is fugitive on wool and silk. Immersing the cloth in this dye stains it blue throughout, but the subsequent washing removes the blueness from the wool and silk, leaving the cotton blue. In this patriotic piece of cloth we now have red silk threads, white woolen and blue cotton. There is now no difficulty in discriminating between these three materials even with the naked eye. Exactly the same principle is used in staining the tissues of animals and plants for examination under the microscope. It is quite possible to select the dyes to such effect that the cell wall may be of one color, the general protoplasm of another, the nucleus in its general structure of still a third, while certain bodies in the interior of the nucleus will come out clearly among them all.

The compound microscope has improved but little in principle since it first came into use. It consists essentially of a magnifying glass in one end of a tube, with another similar but smaller glass at the opposite end. These are so arranged with reference to each other that the first forms an enlarged image which the second again magnifies. Refinement of lens-grinding and added

conveniences of holding parts of the instrument have slowly changed its detailed form, but very little fundamental difference has as yet crept in. The higher the power of a microscope, the greater the curvature of its front lens, and consequently the smaller its size, so that when we come to need magnifications of a thousand times or more, the front lens is very small and admits but little light. Some of this little light is lost as it passes out of the object through the air into the lens. Modern practice fills this gap when higher powers are used with a drop of an oil whose refractive effect on light is the same as that of glass itself, and this avoids the loss which comes of breaking into the air and back into glass. Such a combination is called an oil-immersion lens.

To these refinements has been added in recent years the practice of cutting the tissue to be examined into exceedingly thin slices. In order to do this, the material to be examined is first saturated with melted paraffin and then allowed to cool in a block of paraffin. This block can be fastened in the clamp of an instrument called a microtome. There a razor approaches the block (or the block approaches the razor) in such way as to slice a wafer of paraffin from the end of the block. The turning of a screw raises the block of paraffin and another stroke gives a new slice of paraffin with the tissue embedded in it. The fineness of the screw and the extent to which it is turned determine the thickness of the successive slices. There is no difficulty in cutting slices thinner than $\frac{1}{10000}$ of an inch. The necessity for this lies in the fact that a microscope portrays a picture which has length and breadth but practically no thickness. That is to say, there is no depth to the picture. Everything must be on one level or escape plain observation, and unless it is very near the level, it escapes observation entirely. Hence the necessity for thin slices, and the higher the power of the microscope used, the thinner it is necessary these slices should be.

The study of chick embryos in Balfour's laboratory in Cambridge, England, led to the introduction of an interesting modification of section cutting. It was found that if the paraffin block was of the right consistency and cut perfectly square, each slice adhered by its edge to the edge of the next slice. Thus a ribbon of paraffin was produced in which the slices followed each other in regular succession. This ribbon could be cut into short strips, fastened upon the microscope slide, the paraffin dissolved out, and a cover-glass cemented over the strips so as to keep them permanently. It was possible in this way to embed a small animal, cut it into serial sections, which could be pasted in order on a succession of slides in such fashion that, studying one section after

another, it was possible to trace the course of any organ throughout the entire length of the body. Such methods of killing, fixing, sectioning, mounting, and staining have made possible the sort of investigation which Weismann has done.

Cells examined by methods such as this prove to have at times an exceedingly complicated structure, particularly in that central part of the cell known as the nucleus. There seems to be a general similarity between the protoplasm of one cell and that of another, though this resemblance is really only general. But there is evidently a very distinct individuality in the nuclei of different cells, and it is in this nucleus that Weismann came to study with infinite pains the processes which led him to his interesting and remarkable conclusions. These changes in the nucleus occur particularly in the cells of rapidly growing tissues, where cell multiplication is constantly taking place. The process itself cannot be viewed under the microscope. Before a cell can be brought under a power high enough to see these changes, it must be killed and stained, and hence the process ends. But if a large number of cells are killed at the same time, some of them are sure to be in one stage of the development and others in still another. By comparing these, it has become possible to imagine the process just as one looking at the film intended to produce a moving picture, without power to project it upon the screen, might still see what the picture was meant to convey. In a cell in its resting stage, the nucleus seems to be simply more or less cloudy. As the time approaches when the cell is to divide, a streaming motion in the cloudiness seems to result in the formation of a long and slender thread. While this process is going on, a little spot near the nucleus itself divides into two spots, each of which moves away from the other in such way that after a while these spots are on opposite sides of the nucleus, while from the spots slender rays proceed in all directions, but particularly through the nucleus. On the sides which are toward each other the rays from these spots meet in the nucleus, forming a spindle. By this time the slender thread which was streaming around the nucleus has broken into separate pieces. These seem to be laid hold of by the threads of the spindle and pulled into position in the center of the nucleus, each piece of the thread being bent into the shape of a horseshoe. Now comes the crucial moment. Each horseshoe splits from end to end into what look like exactly similar halves, and the two halves move away from each other toward opposite sides of the nucleus. Thus the material which had formed the streaming thread has been slit into half from end to end and the fragments have collected in opposite ends of the

nucleus. The wall of the cell now begins to send a partition through the center of the cell, thus breaking it into two cells, each with a nucleus of its own, just like the nucleus in the other end of the cell, because its material has been so exactly divided by this intricate process. Weismann suggests that when this division occurs, the action is taken which determines that the daughter cell shall inherit the qualities of the mother from which it is separated. He believes that strung on this thread is a long series of what he calls determinants, each of which decides some point in the development of the cell. Here, then, is the mechanism of heredity. The reason why the offspring resembles the parent is because the cell from which it sprang, the egg cell, had been detached from the cell which produced the parent and shared its determinants.

It is clear, however, that the ordinary animal shares the qualities of two parents. If he were to have all the determinants from both parents, it is evident that he would have twice as many as either of them. In the next generation this number would be doubled again, until the animal's cells would be thoroughly cluttered with determinants. It is an easily recognized fact that a child resembles one parent in one respect and the other in another. The reason for this Weismann has again interpreted to us. Just before an egg is ready to be detached and sent out into the world its nucleus goes through what is known as a reducing division. Instead of taking one half of each section of the thread, the cell divides in two, one part taking one half of the threads, not as before one half of each thread. By this process, the cell loses one half of its possibilities of resembling the parent or the parental line from which it was detached. This reducing division occurs both in the egg detached from the body of the mother and also in the sperm cell as detached from the body of the father. When now the egg is fertilized, that is to say, when the egg cell of the one parent fuses with the sperm cell of the other parent, the number of determinants rises once more to the full quota. The offspring has as many possibilities as either parent, but half of its possibilities have been derived from one parent and the other from a different parent. Accordingly, the new individual will be a fresh combination of traits from both parents. By the time Weismann had become entirely familiar with the facts of cell multiplication, he had worked so closely that his eyes were seriously affected and from this time on he could not do very much microscopic work. This, however, gave him abundant time to think over the work he had already done, and it was this reflection quite as much as the preceding work which has made Weismann famous.

There are several important truths which have become pretty well established. The first, and one of the most remarkable conclusions to which Weismann came, was that an animal does not produce eggs. The animal grows from an egg. While it is growing from an egg, all the eggs it is ever to lay are growing inside of it, direct from the preceding egg. Accordingly, the egg is not produced by the parent. Both parent and egg are produced from the preceding egg and all the parent has to do with the egg is to fatten it up and send it out. This is a very important fact, and if true,—and there seems little possible doubt of the truth of it,—it becomes evident that the parent simply enshrouds, protects, and nourishes and does not produce the eggs. Accordingly, what happens to an animal during its lifetime can have no effect upon the qualities of its offspring. These are decided at the same time that the qualities of the parent are decided, so far at least as is decided by the determinants which are not thrown away. This has given rise to Weismann's famous law that there is no heredity of acquired characters. What that means is this: Suppose a horse to have had two or three colts before it was discovered that the parent horse had splendid trotting qualities. He is now put into training and transformed into a fast trotting horse. Subsequent to this, he has several more colts. These last colts have no more possibilities of being fast trotters than have those produced before the horse ever thought of trotting. Indeed, these last have no more chance of becoming trotters than if the qualities of the parent had never been discovered or exercised and he had plodded all his life in front of a plow to which he was ill adapted. It is the fact that he has racing stuff in him and not that he is a racer, which makes him the valuable sire of trotting horses. Of course, a son may seem to resemble his father because he has learned to imitate his habits, but this is a very different process.

A second of the teachings made clear by Weismann is that we do not receive qualities from our parents, but the determinants of those qualities. If I inherit from my father a house, he hands over to me the house which was his. It is a very different process when I inherit the blue eye of my father. He does not hand his over to me. He does not give me eyes at all. I receive from the same egg he did one half of the same determinants, the other half of which gave him blue eyes. The determinants, then, enable me to develop qualities like those of the parent.

Another, at first sight almost startling, conclusion of Weismann's is that we have two parents not because they are necessary to reproduction. This

often happens in lower animals by a single parent. But double parentage provides that the new creature shall have qualities different from any previously existing creature of the same kind, because it has a new combination of the qualities of the two parents. It is said to be so nearly impossible to shuffle and deal a pack of cards exactly the same way twice, that one might spend his entire life shuffling and dealing and never accomplish this end. But the possibilities of development in the human species are far greater than the possibilities of shuffling in a pack of cards, and the probability of two persons being exactly alike is so slight that it probably never occurs, excepting in the case of identical twins, who have in reality developed from two halves of the same egg.

It is most interesting to find that Mendel's law, with its dominant and recessive characters, its pure lines and its hybrids, is true for peas. The question naturally arises how far does it hold in other realms. Hosts of research workers are now carrying this problem into all sorts of fields. Guinea-pigs and rats, pigeons and chickens, are showing us in one way or another that they too obey Mendel's law. The most interesting question of all is, of course, in how far man finds himself under the same inexorable law. The literature of heredity in the human race is a doleful one. It has to do with diseases and deformity. The reason for this is plain. Diseases and deformities, when at all unusual, impress themselves so thoroughly that they are remembered to the third generation, while more amiable qualities or slighter peculiarities are entirely forgotten. We do not yet have records enough to carry the investigations very far. This is now being remedied, and after a while we shall understand human heredity as well as we do that of the guinea-pig or of peas.

Meanwhile, there is one easily observed respect in which Mendel's law seems to work out very clearly in human beings. The color of the iris of the eye is due to one or two factors, as the case may be. If the coloring is entirely due to pigment at the back of the iris, the eye will be blonde; blue if the iris is thin, and gray if it is thick. If, on the other hand, there be coloring matter on both front and back of the iris, then the eye is brunette to a greater or less degree. Now the brunette eye is dominant over the blonde, hence you can never tell whether the children of a brunette-eyed parent will be blonde or brunette, because there may be a recessive blonde under any brunette and it not show except in the offspring, but a blonde-eyed parent cannot conceal brunette character because if present it would be dominant and hence show. Accordingly, two brunettes of pure brunette ancestry will have only brunette

children. If, however, each of them has one blonde parent, their children will probably be some of them blonde, others brunette, in the proportion of three brunette to one blonde. If a pure blonde and a pure brunette are married, the children will all be brunette, but the grandchildren may be some of them blonde. Two blonde-eyed parents can have only blonde children. It may seem at times as if this law did not quite carry, but when it does not, inspection will usually show that what was thought to be a blonde eye is really flecked with brunette spots or has a brunette edge about the pupil.

As yet our knowledge of heredity in the human race is too slight to be of much practical importance except to make us wonderfully loath to see any feeble-minded individual produce children. In other fields, however, the chicken fancier, the animal breeder, and the man in search of new types of plants have clear guidance that is bringing immediate practical and valuable results.

ETHER WAVES AND THE MESSAGES THEY BRING

LESLIE BIRCHARD SEELY

Delivered December 20, 1916

HOWEVER interesting it might be to do so, it is not possible for us at this time to trace historically the progress of knowledge which has made possible the assumption implied in the first word of our subject. That ether exists has come to be commonly accepted as a fact. The transmission through space of energy by wave motion would be impossible in the absence of some all-pervading medium. The universal acceptance of the wave theory of light thus carries with it the tacit recognition of the fact that luminiferous ether exists.

The ether-wave theory, applied first to light, the only form of this energy which appeals directly to our senses, has been extended gradually until it now includes a wide range of wave energy which may be detected only indirectly. We cannot go either into the history of this development or into the proofs of the existence of the ether waves themselves, except incidentally. We must confine ourselves for the most part to a mere description of the waves and to some of the more important facts which they have revealed, or, as our subject has it, the messages they bring to us. It might be well to state, however, that these various forms of ether energy have been ascribed to wave motion because they exhibit interference, resonance, and other properties and phenomena known to exist only in waves.

Two of the things we must speak of most frequently in our description of ether waves are wave lengths and frequencies. By a wave length we mean the distance between any phase in one wave to the same phase in the next wave following or preceding. Now the wave length of these waves is exceedingly variable, being in some cases so minute that a special unit has been devised for their measurement. This is called the Ångström unit and is one ten-millionth of a millimeter. That means that two hundred and fifty thousand of these units make approximately a thousandth of an inch. Other waves are measured in miles. By frequency we mean the number in a train of waves which passes a given point in a unit of time, *e. g.*, in a second. Of these waves, all lengths seem to travel at the same speed; thus the frequencies are inversely proportional

to the wave lengths, and vary from perhaps a few thousand per second to hundreds of trillions per second. Since light waves are the best known of all of these, let us begin our study with them and then, as time permits, take up those less well known.

It is commonly known that a beam of white light is composed of trains of waves of differing wave lengths, and that if the beam is passed through a prism and bent considerably out of a straight path, the waves of different lengths will be separated, since the short waves are bent more than the long ones. You can see on the screen (Fig. 1, A) the effect of thus separating out the dif-

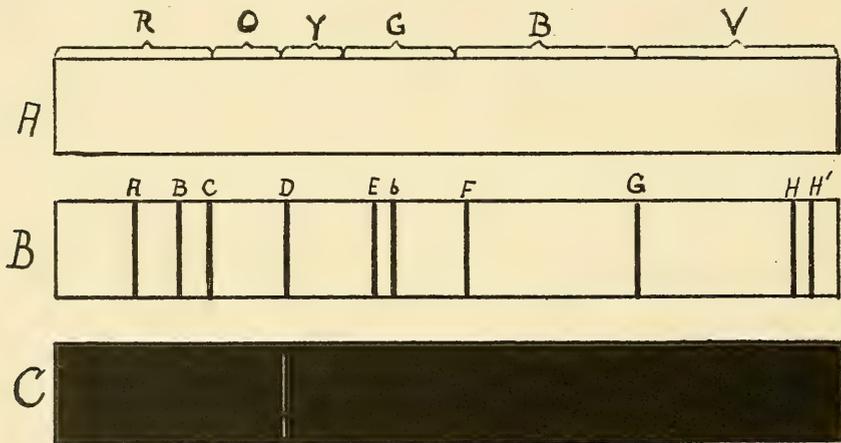


Fig. 1.—A, Continuous spectrum; B, solar spectrum, showing dark lines; C, bright-line spectrum of sodium vapor.

ferent wave lengths. The red represents the longest, the violet, the shortest, visible waves in the beam. Those of intermediate length lie on the screen between the red and the violet, orange, yellow, green, and blue. Now by several methods, depending on the principle of interference, the length of the waves producing these various colors can be accurately measured. The deepest red ones are about 7800 Ångström units, the shortest violet about 3800 Ångström units in length. Ether waves lying within these limits are the only ones visible to the human eye. Others do not reveal themselves to our unaided senses, but must be detected by some other means. We shall speak of these others later; there are many of them. For the present, however, I wish to consider the visible waves and a number of interesting facts they have revealed to us.

The best method of studying these dispersed rays or spectra, as they are

called, is by means of the spectroscope. This is an instrument in which the dispersed beam is introduced into a telescope, thereby enabling the observer to view the spectrum greatly magnified. By means of the spectroscope it has been found that spectra are not all alike, but fall into three general classes, each determined by the source from which the light has come and the treatment it has subsequently undergone. For instance, if the light coming directly from a glowing solid or liquid, such as the white-hot carbons of an arc light or a mass of molten metal, be viewed through the spectroscope, the spectrum is continuous from the red to the violet (Fig. 1, A). This simply means that the light from such a source contains all possible wave lengths from 3800 to 7800 Ångström units. This is called a continuous spectrum. If some gaseous substance, however, is heated to incandescence and the light given off be dispersed, the spectrum is not at all continuous, but consists usually of a few bright lines of color. This can only mean that but a few wave lengths are present in such light. This forms a spectrum such as you see on the screen, and is called a bright line spectrum (Fig. 1, C). Now a remarkable fact about this phase of the subject is that each gas has its own set of lines which are characteristic of that particular gas. Thus sodium always gives off yellow light, which is made up of two slightly different wave lengths, and consequently always produces a spectrum of two lines lying close together, known as the D lines. In a spectrum where the dispersion is moderate these lines are so close together as to appear as one line (Fig. 1, C). Hydrogen has a very complex spectrum, but one that is entirely characteristic. In the same way calcium, potassium, barium, iron, and, in fact, every other substance when volatilized and made incandescent, produces a characteristic bright line spectrum. This is the fact upon which the spectrum analysis of the chemist depends. He places in a hot flame the substance to be studied, and it is heated to incandescence after having been vaporized. Then passing the light through the slit of the spectroscope he determines the material present by identifying the groups of lines in the spectrum thus produced with the lines known to be produced by the various known substances. As may be imagined, this method of study has been a powerful aid in determining the substances to be found in the sun and other celestial bodies; for if any gas from a terrestrial source produces always a certain set of bright lines and those lines cannot be produced in any other way, we are justified in assuming that when those same bright lines are produced by the light from a celestial source, the same gas is present in that source.

If the light from a glowing solid or liquid which, as we have seen, contains all possible wave lengths of light, be passed through a gas, it emerges apparently lacking those wave lengths which the gas itself produces. Thus if hydrogen be studied, it will be seen to produce in the spectroscopie a certain set of bright lines. If the light from a glowing solid or liquid be passed through hydrogen, it will be seen that there are dark lines just where the bright lines of the hydrogen spectrum were. Such a spectrum is called an absorption or dark line spectrum (Fig. 1, *B*). It is found that these dark lines are dark only in comparison with the light areas produced by the solid; for the waves produced by the gas are there, but the gas, being at the lower temperature, produces wave trains not nearly so intense as those it has absorbed.

The three kinds of spectra possible, then, are: continuous ones, formed by the light from a glowing liquid or solid; bright line spectra, from glowing gases; and dark line spectra, formed by passing light from a glowing liquid or solid through a gas, the gas being usually at a lower temperature.

Much of our knowledge of the composition of the sun and stars is based on the facts just set forth. You see on the screen a representation of the spectrum formed by sunlight (Fig. 1, *B*). Notice that it is a dark line spectrum. The spectra of the stars are of the same sort. We conclude, therefore, that the sun and stars are solid or liquid masses, glowing hot, surrounded by atmospheres of gaseous material. The spectra of the nebulae are entirely different, being bright line spectra. This shows that the nebulae are masses of gaseous material without any solid or liquid core. In the Milky Way in some places it is impossible to tell, even with the most powerful telescope, whether the luminous areas are multitudes of stars set so thickly that the telescope will not separate their individual images, or whether they are enormous masses of incandescent gases. The spectroscopie settles the matter instantly. Turned upon some of these luminous areas we get a dark line spectrum, indicating vast masses of stars each having a central core of solid or liquid material. From others we get a bright line spectrum indicating the presence merely of vast bodies of incandescent vapors.

If we study carefully the solar spectrum, we find that it presents a very large number of dark lines. Fraunhofer, who first made a careful study of these lines, counted and mapped about 700 of them. They are called after him, Fraunhofer's lines. Many more have been discovered since his time, there being now about 12,000 of them which are not identified with the known lines

of any substance known to exist on the earth. Since these lines are formed by the absorption of certain wave lengths from light which would form a continuous spectrum, it is possible, by a study of them, to tell what gases the light has passed through. On the screen you see a part of the solar spectrum superimposed upon the spectrum of iron vapor (Fig. 2). You will note that the coincidence of the bright lines of the vapor spectrum with the dark lines of the solar spectrum is perfect. This seems to be positive evidence that the vapor of iron is present in the sun's atmosphere. Kirchhoff has shown that the coincidence is complete for the 460 bright lines known to exist in the spectrum of iron vapor. It might be thought that the coincidence is merely chance, since such a large number of these lines exist in the spectrum of the sun. Kirchhoff calculated that the odds against mere chance in the matter are a million million millions to one. By the same method a great many elements have been discovered in the sun, among them H, Fe, Ca, He, Mg, Ni, Zn, and Cu. It might

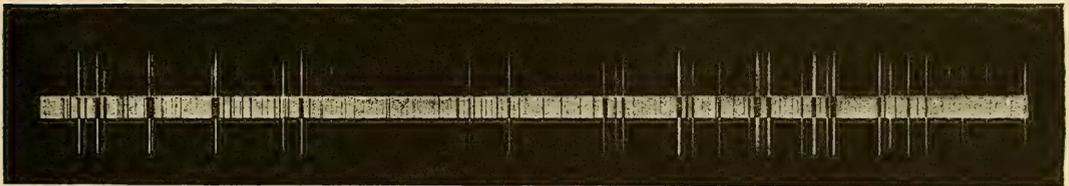


Fig. 2.—Solar spectrum with superimposed iron spectrum.

be noted that Au, As, Hg, N, and S are some of the common ones found on the earth which have not been found there.

In the same way the light of the stars has been studied and much interesting information gathered concerning the elements of which they are composed.

But this is only the beginning of the statement of the interesting facts concerning celestial bodies which these ether waves bring to us. To understand fully some others it is necessary to discuss at this point a principle in wave motion known as Doppler's principle.

In the upper line of the diagram on the screen (Fig. 3, *A*), let us suppose an observer stationed at *A* while a body producing waves is at *B*. We will suppose that the body produces ten waves per second, and that the distance *AB* is numerically equal to the speed of the waves expressed in units per second. Then at the end of one second the first wave will have reached the observer and the tenth wave will have just been produced at *B*. The distance between

A and B will be occupied by these ten waves and one wave length will be one-tenth of the distance AB . But if the body be moving away from the observer so that, having started from B of the second line, it reaches B' at the end of one second, the ten waves will occupy the longer distance AB' . Each wave length will be one-tenth of AB' , and therefore greater than when the body was stationary at B . Again, if in the lower line the body move toward the observer while producing the waves, going from B to B' in one second, the wave length must be shorter than in either of the other cases. Thus, in sound, if a locomotive be moving toward one as it whistles, the sound waves must be shorter and therefore the sound be higher in pitch than if the locomotive were stationary. Likewise if the locomotive be moving away from the observer the sound must obviously be of lower pitch.

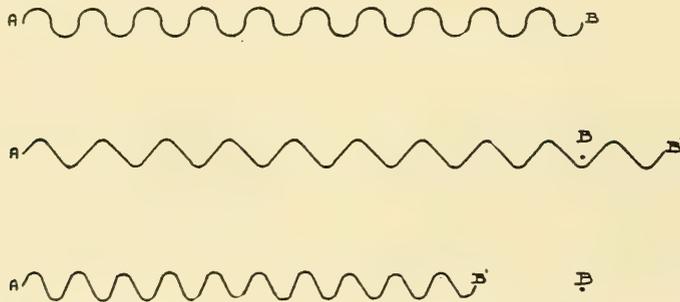


Fig. 3.—Diagram illustrating Doppler's principle.

To understand the application of Doppler's principle to spectroscopy it is only necessary to remember that the position of the lines in the spectrum depends upon the wave lengths represented. Therefore if there is a change in the wave lengths there will be a shift in the position of the lines concerned. Consequently, if a luminous body is moving away from us, the length of the waves will be increased and the spectrum with its lines will be shifted in the spectroscope toward the red end, while if the body be moving toward us the shift will be toward the end of the shorter waves, or the violet. Consequently a shift from the usual position of any characteristic set of lines may be used for the determination of the speed of the source of the light toward us or away from us. Many interesting facts have been established as a result of this method of study. It has been used to calculate the speed of different portions of the sun, such as the gases in the neighborhood of sun spots, or the tongues of flame—the prominences—which shoot out from the central body sometimes at a speed

of 700 miles per second. Also it has been used to estimate the speed of stars whose distances from the earth is entirely too great for it to be gaged by any other method. A study of the stars from the point of view of this principle has revealed the fact that on one side of the sun a majority of the stars seem to be approaching it, while on the other side a majority are receding from it. This can be interpreted only as evidence that the sun is really moving through space toward the side on which the stars seem to be approaching it. Also this principle has helped to reveal the structure of some of the heavenly bodies; for instance, Maxwell, by means of mechanical considerations, showed in 1859 that the rings of Saturn could not be solid. The spectroscope reveals the fact that they are either solid or liquid. It remained for Keeler to show, in 1895, by the application of Doppler's principle, that the inner edge of the rings is moving faster than the outer edge. As Maxwell had indicated, the rings are composed of meteorites each moving separately as a satellite about the planet.

So much in a very hurried way for Doppler's principle and its application to ether waves. There is another device for reading the messages brought by the visible waves which we ought to consider, then we will pass on to the invisible spectrum. The device to which I refer is the spectroheliograph. Let us suppose that a telescopic image of the sun be formed in the plane of the slit of a spectroscope. Obviously the slit may be placed in any portion of the image, and when in any particular portion, it will admit into the spectroscope light only from that part of the sun whose image falls on the slit. If there is, for instance, calcium vapor in that portion of the sun, then the calcium lines produced in the spectroscope will reveal that fact. Now let us suppose that the spectrum formed by the spectroscope be received on a screen and a second slit be made directly in one of the calcium lines. Then a photographic plate placed in this second slit will have formed on it an image of that part of the image of the sun which falls on the first slit, provided that this particular wave length is being produced by the corresponding portion of the sun. Now if slit No. 1 be moved slowly across the image of the sun, and at the same speed the plate behind slit No. 2 be moved sidewise, there will be found on the plate a continuous image of the portions of the sun which have given light to the first slit. This image of the sun will represent it as photographed by the particular wave length of the calcium line which has been used. In other words, it plots out the areas of the sun which have calcium producing the particular wave length used. In the same way, if slit No. 2 be made in a

hydrogen line, the hydrogen areas of the sun will be photographed, and so for any gas whatever. Now this method of study has led for the first time to an accurate knowledge of the distribution of gases in the atmosphere of the sun, particularly of the enormous quantities of hydrogen and calcium in the regions about sun spots. Also by this method it has been determined just what are the gases forming the gigantic flames shooting out from the sun's orb. These formerly were studied only at times of eclipse, when they were visible as prominences on the perimeter of the disk. Now they can be studied and photographed on the face of the disk at any time. Ordinarily the light of the orb is much too brilliant for them to be detected, but by the spectroheliograph all other light except just the wave length to be studied is eliminated.

It is found in the laboratory that most gases, while they produce perfectly characteristic spectra, will, under certain conditions of temperature, pressure, and electric potential, produce lines which otherwise are extremely weak or perhaps entirely lacking. For instance, if calcium vapor is dense and hot, a certain line close to the K line comes out strongly; while if it is comparatively rare and cool, this line is missing. By setting the second slit of the spectroheliograph in this line we get a picture of the sun's atmosphere at a lower level than if we were to select a line which represents the gas at a lower temperature and pressure, for it is clear that the gases become rarer and cooler as we approach the upper layers of the sun's atmosphere. The same reasoning applies to the spectroheliograph pictures made in the lines of any other gas which shows the same behavior, *e. g.*, hydrogen. In this way it is possible to explore the atmosphere of the sun at different levels—a truly marvelous achievement.

Thus we see that light brings to us the knowledge of many facts besides those which it reveals directly to the eye. Now let us consider briefly some of the other sorts of ether waves.

If, when a beam of sunlight is dispersed by a prism, we place a thermometer or a thermopyle just beyond the red end of the visible spectrum, we discover that the temperature is higher in this region than on other portions of the screen. This is explained by the statement that in sunlight there exist waves longer than any of those that affect the eye. These longer waves give rise to heat energy when they are intercepted by the screen, or in fact by any body which is not transparent to them. Closer study reveals the fact that all bodies, even at ordinary temperatures, are giving off similar waves, but probably

of much greater wave length than any found in the solar spectrum. As the temperature is increased the waves become shorter and shorter, until at about 525° C. the first red waves appear, and at from 800° to 1200° C. bodies have reached a white heat. These infra-red waves—so called because of their position in the spectrum—obey the same general laws as light waves. They are refracted, reflected, and absorbed, and exhibit the phenomena of interference and resonance. They travel with the speed of light. They have been made the subject of special study by Rubens and von Baeyer of Berlin, and are found to range in length from 8000 to 3,000,000 Ångström units. This latter length is equal to 0.03 cm.

If an electric spark is passed between the terminals of an induction coil or between the coatings of a Leyden jar, light, of course, is produced. The effect of this light on the eye is that of a single flash of very short duration. A suitable photographic apparatus shows, however, that what seems to be a single flash of light is in reality a succession of light pulses of very much shorter duration, caused by the oscillation of the discharge between the knobs. These oscillations set up in the surrounding ether waves very much like light waves, but much longer than any we have thus far mentioned, ranging from about 0.3 cm. to thousands of meters in length. These are the waves used in wireless telegraphy. Hertz first identified them as waves by showing that they exhibited the property of resonance. He also showed that they traveled with the speed of light. From him they are known as Hertz waves. Since the longest infra-red waves are 0.03 cm. long and the shortest of the Hertz waves are about 0.3 cm. long, it follows that there is between the two a belt of unknown waves if we assume that the spectrum is entirely continuous.

As I have said, the Hertz waves are used in wireless telegraphy. An aerial consisting usually of a large grid of wires is suspended high in the air. As a train of these waves passes it, the aerial is engulfed in the alternate high and low potentials which constitute the wave train. Therefore the aerial itself alternates rapidly in potential. If the aerial be connected to the earth with its constant potential, it is clear that an alternating current of high frequency will exist in this connecting wire as the wave train passes. As the wave train is produced in a spark-gap possibly hundreds of miles distant, it is clear that we have here the foundation of a system of communication between the spark-gap and the ground wire of the aerial. Some device for detecting and recording

the currents in this ground wire is the important piece of apparatus in all wireless work.

The Marconi coherer was one of the first as well as one of the simplest of such devices. Although it is now obsolete, it illustrates well the use of these waves for wireless telegraphy. The metal plate *A* (Fig. 4) is a resonator and corresponds to the aerial in a working wireless set. A wire runs from this plate to the coherer, *C*. This consists of a glass tube nearly filled with a mixture of iron and nickel filings, which are held in place by a small stopper at each end of the tube. The wire from the aerial runs through the stopper at one end

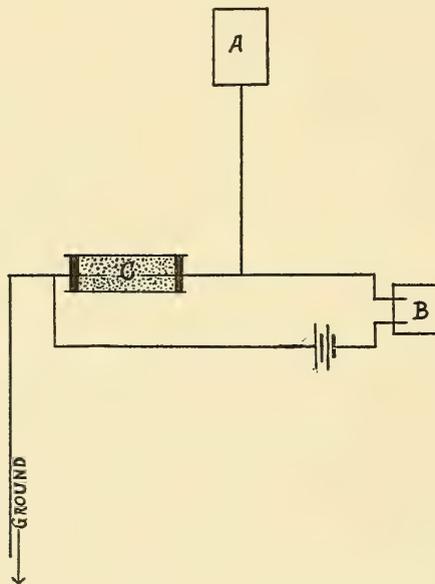


Fig. 4.—Diagram showing use of Marconi coherer.

and is buried in the filings. Another wire runs from the other end of the tube to the earth. The ends of the wires in the tubes are separated by about one centimeter of the loosely packed filings. An ordinary bell circuit with two cells in it also passes through the coherer, using the same terminals at the tube as the aerial. Now ordinarily the resistance of the filings is so great that the bell will not ring. If, however, an electric spark occurs, even at some distance, the alternating current set up in the wire from the aerial causes the filings between the two wires to cling together and the resistance is so diminished that the bell will ring. A device like the clapper of an electric bell, working in the same circuit as the bell and tapping the tube, shakes up the filings and stops

the bell as soon as the spark is discontinued. In this way the ringing of the bell can be controlled by a person operating the sparking apparatus. The Morse code may be represented by a suitable arrangement of long and short rings.

If, when a solar spectrum is thrown on the screen, a photographic plate is placed beyond the violet end of the spectrum, it will be found that the plate is quickly affected. This fact reveals the presence of waves shorter than those we call violet. They are called the ultra-violet waves. They are always produced at very high temperatures, and may easily be obtained by passing a violent electric discharge through a body of gas at low pressure. The Cooper-Hewitt mercury vapor lamp produces them in large quantities. These waves were extensively studied by Draper, Stokes, Cornu, and others. It soon became apparent that the greatest difficulties in connection with their study lay in the fact that they are absorbed by comparatively thin layers of glass or even of air; therefore, they must be studied in a vacuum if satisfactory results are to be obtained, and with lenses and prisms of some other material than glass, usually quartz, or better still, fluorite. In the extremely short lengths, Lyman has been very successful in replacing both lenses and prisms by a concave reflection grating. The men I have mentioned first extended our knowledge of the ultra-violet to about wave length 2000. Then very little additional was done until Schuman took up the work. Our accurate knowledge of this region is due largely to the work of this one man. His results were so remarkable and were obtained under such conditions as to make appropriate a few words concerning him. He was born near Leipzig in 1841, and was educated as an engineer. He engaged in the business of manufacturing machinery for book-making. He continued in this business until 1892. He was unable to engage in scientific work until after he was forty years of age. Even then his investigations were carried on in the evenings and at such other moments as he felt he could spare from his profession. He was never wealthy, and most of the proceeds of his day's work was devoted to his investigations. Under his persistent application his health was undermined and his eyes became seriously affected. In 1903 he was forced to give up all experimental work and in 1913 he died a martyr to science. He instituted the method of working in a vacuum and substituted fluorite for prisms and lenses. He extended the spectrum to about the region of 1250 Ångström units, and studied the properties of the region to this point very thoroughly.

During the last twenty years the subject has been studied by Lyman, of Harvard University. He has accurately measured waves to the length of 600 Ångström units, and discovered others still shorter.

Some of the properties of these waves have been mentioned as we have described their study. They are easily absorbed. Very few of those coming from the sun reach the surface of the earth, being absorbed by the upper layers of the atmosphere. A very thin layer of glass absorbs a large percentage of the waves above 3000 units in length, and almost entirely the shorter ones. The waves in the region of 3000 units possess to a remarkable degree the power to ionize air and other gases. Only a few of these waves reach the surface of the earth from the sun, but it has been shown that a large number of them do reach the cloud levels of the atmosphere. It has been shown by C.T.R. Wilson and others that ions of air may act as condensation nuclei in cloud formation. Probably, therefore, these waves play a great part in the formation of rain drops, particularly in the higher cloud levels, where there are comparatively few dust particles. One of the most remarkable properties of these waves, particularly in the Schuman region, is their bactericidal action. If some mobile form of cell life be placed in the field of a microscope and be observed while subjected to ultra-violet light of about 1850 units in wave length, the killing action is seen to be almost instantaneous. Not only is the organism killed, but its body is in some cases absolutely torn apart. This abiotic action is not confined to micro-organisms, all cells being more or less susceptible to it. Thus it will produce inflammation of the eyes and of all the mucous tissues of the human body. It is probably true that without the shielding action of the atmosphere all life on the earth would be stamped out. The rather fanciful theory that low forms of life might be transported through interplanetary space is seen to be untenable in the light of these facts. It is obvious that as these pass through this space they must be killed.

If we pass another unknown belt in the spectrum in our progress toward the shortest waves to be found there, we come to the x -rays (Fig. 5). These were first discovered by Roentgen in 1895. It had long been known that when an electric discharge is passed through a highly exhausted tube there is a stream of energy thrown off from the cathode. This is called the cathode ray. It is now known that this ray is a stream of negatively charged particles called electrons. Roentgen showed that if these particles be allowed to strike upon a target of some heavy metal there would be given off from this target rays

which were able to affect a photographic plate through glass, paper, flesh, and even thin layers of metals. This discovery created a great stir among scientists, and before long many men were working on the subject. It is not my purpose to trace the development of our early knowledge of these rays, nor their application to photography and medicine. I do, however, wish to demonstrate their power of penetration. The waves themselves are much too short to be detected by the eye, but, allowed to fall on certain substances, such as platinum barium cyanid, they produce a fluorescence which can be seen. Now, if any object be passed between the tube and the screen, they will or will not reach the screen, depending upon whether or not they are able to penetrate the interposed substance. A small body which they cannot penetrate will cut

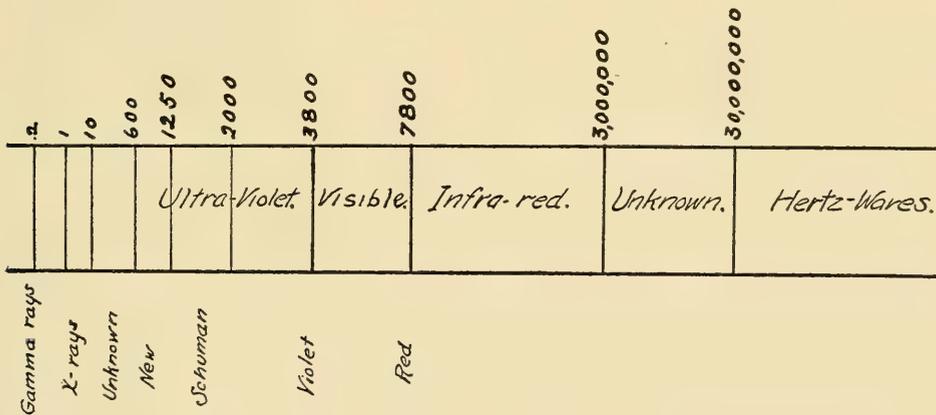


Fig. 5.—Diagram, not drawn to scale, of spectrum, including all known ether waves. Wave lengths are given in Ångström units.

them off from a part of the screen and that part of the screen will not fluoresce. Thus the body is seen, in effect, by its shadow on the screen. If the screen be replaced by a photographic plate, a picture may be made of the shadow.

For about seventeen years these rays were used and studied without knowing their exact nature. In 1912 Dr. Max Laue, of Munich, identified them as ether waves of very short wave length. His method will be clear if we refer for a moment to the principle of diffraction in light. If a beam of light be passed through a grating made by ruling on glass many fine parallel lines equally spaced, a spectrum is produced which is for all purposes like that produced by the prism. In order to be effective the grating must have in general lines so close together that the distances between them are of the same order of

magnitude as the wave length of the waves to be studied. Rowland, of Johns Hopkins University, ruled these gratings very successfully and they are much used in the study of light. Now it occurred to Laue that if he had a grating whose spacings were small enough, a spectrum of x -rays could be produced, provided they were, as he suspected, ether waves of very short wave length. The limit of physical possibility seemed to have been reached in the ruled gratings, but it seemed to Laue that if the molecules of crystals are arranged in planes, these planes might easily be so close together that their edges could be used to diffract the x -rays. Experiment proved that he was correct. Using the experimental results he obtained, he computed the wave length of the x -rays to be from 1 to 10 Ångström units. This means that 1000 of them would be about equal to the length of one light wave. In a few months after these results were published Mr. W. L. Bragg, of Cambridge, England, announced that the x -rays could be reflected from the face of a crystal. It is found that crystal reflection differs from mirror reflection in that any given wave length can be reflected only at certain angles. In this way the crystal separates the various wave lengths in a beam of x -rays and arranges them in a spectrum. Making use of this sort of x -ray spectroscopy, Bragg found that the various elements have characteristic x -ray spectra, just as they have characteristic light spectra. The x -ray spectra of the various elements have been studied and the elements classified according to them. The elements arrange themselves in a certain order when thus classified, which is the same as their order in the periodic system. Thus if the position of an element in the periodic system be known, its radiations in the x -ray spectrum may be foretold, or, on the other hand, if its x -ray spectrum be known, its position in the periodic system has been determined. It has been stated that the x -rays of a given wave length are reflected from crystals only at certain angles. These angles are determined by the wave length and the distance between the planes of the crystals. If any two of these are known, then the third can be determined by a simple mathematical formula. Therefore, knowing the wave length of a beam of x -rays and the angle at which it is reflected, it is possible to determine the spacing of the planes in the crystal.

The intensity of the reflected x -rays gives a clue as to whether the planes are made up of light or of heavy atoms, for the heavier the atoms, the more penetrating the reflected rays will be. Thus it is possible to show by the action of the x -rays on crystals not only the spacing of the planes, but the arrange-

ment of the atoms in the planes. For instance, if a crystal of sodium chlorid be cut so that the surface lies in a plane parallel to any of its three axes, the reflected rays show that the surface is composed of equal numbers of sodium and chlorin atoms. If, however, a surface be made in a plane cutting off equal intercepts on the three axes, we find the surface to be composed entirely either of sodium or of chlorin atoms. The diagram on the screen (Fig. 6) shows the only arrangement of atoms which will fulfil these conditions. The dots may be considered as representing chlorin atoms, while the rings represent sodium atoms. It will be seen from the diagram that instead of any one sodium atom being associated with a particular chlorin atom, as would be supposed from the chemical symbol for the molecule, it is associated equally closely with any of six such atoms. Thus the notion of molecular structure as applied to crystalline solids apparently does not hold, but is replaced by a mass structure in which the proportion only of the elements is indicated by the chemical formula. About forty inorganic crystalline substances have been studied, and in each case similar results have been obtained. There is no evidence, however, that these results hold for organic or for non-crystalline substances. Just what future developments along these lines may bring forth cannot be predicted.

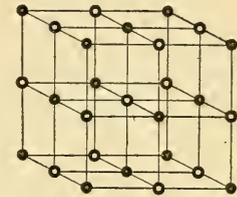


Fig. 6. — Diagram showing arrangement of atoms in crystal of sodium chlorid.

It will be seen from what has been set forth that all these manifestations of energy in the ether have been reduced to a single form of wave motion, since they differ essentially only in wave length and in frequency. This work constitutes one of the two greatest achievements in science during the past hundred years. As a result of it the electromagnetic theory of light has been firmly established, and many apparently diverse problems have been merged with those greatest of mysteries confronting physical science—the nature of ether, and the structure of, and the relations between, matter and electricity.

THE CHEMISTRY OF BREAD-MAKING

CHARLES H. LAWALL

Delivered March 19, 1917

THE chemistry of bread-making is a subject which depends for its scope much upon what is considered as the limiting definition of bread. In the broadest and figurative senses bread may be understood to mean all food-stuffs eaten by man. In a more restricted sense it may mean a food made of any kind of flour or meal, as wheat bread and corn bread. In the present study it is understood as the product from wheat or rye, baked into loaves or smaller individual portions termed rolls, biscuits, etc., and of a porous or vesicular character, giving it the quality commonly known as lightness.

The word "bread" is comparatively modern, but etymologists differ as to its origin, some holding that it is derived from the same root as "brew," others that it comes from a Teuton word meaning a fragment or piece; the latter view is supported by the fact that in all Teutonic languages the original word for bread is equivalent to our word "loaf."

Bread-making dates back to the earliest records of uncivilized man, the Swiss lake-dwellers of the stone age having been found to be acquainted with the making of a crude form of unleavened bread. This compact form was probably the earliest known, presumably sun-dried at first, and later baked in hot ashes or on hot stones. The hearth naturally evolved into the oven, which was known to the Chaldeans about 2500 B. C. The Chinese attribute to one Ching Fong, who lived about 2000 B. C., the art of husbandry and the method of bread-making from wheat. The Egyptians greatly improved the art, and were familiar with the use of wheat, barley, and other cereal flours. The Greeks attributed the origin of bread to Pan, the god of pastures, forests, and flocks, whence our word "panary," commonly used in the phrase "panary fermentation" as applied to bread. The Romans still further developed bread-making, and it is in their time that the first reference to public bakehouses is found. Hebrew writers refer to both leavened and unleavened bread, as does also Pliny, who differentiates the former into the kind in which wine "must" is used as the leavening agent, and that in which the "barm," or yeast from beer brewing, is used.

The classification into leavened and unleavened breads affords a sharp distinction. The latter type is exemplified by the Matzoth, or Passover cakes, consisting of flour and water made into thin cakes and baked, and also the various types of crackers or biscuits, as they are usually called by the English, which generally have salt and shortening (fat) present. The chemical changes in unleavened bread and crackers are almost negligible. Beyond a limited alteration of the starch to dextrin in some cases no chemical change takes place, but the starch granules swell.

The leavened bread, which is distinguished by its cellular or vesiculated structure, is capable of subdivision into three groups, so far as preliminary methods of preparation of the dough are concerned, and into many varieties, depending upon composition and methods of baking. The three essentially different methods of preparation are: 1, Leavening the dough by aëration by mechanical means; 2, leavening the dough by the employment of chemicals which react to evolve a gas; 3, leavening the dough by the action of yeast or bacteria. These three classes must be studied separately, so far as many of the chemical changes involved are concerned, and will form the basis of the present essay. The varieties into which bread may be divided are more easily specified than precisely distinguished. *Wheat bread* may be white bread, which is made from white bolted flour; *Graham bread*, so named from its originator, who made it from a mixture of whole wheat flour and white flour; or *whole wheat bread*, which is made from a straight unbolted flour containing all the bran. White bread may be of the French or Vienna type, which, being baked in an oven containing steam, has an additional alteration of the surface starch to produce the characteristic amber glaze on the outer surface. This is often imitated by applying a wash of beaten whole eggs just before the bread is placed in the ordinary oven.

Graham bread is sometimes called *brown bread*, but the latter term ordinarily applies to a cake-like product, largely eaten in New England, made from wheat flour and corn meal, with molasses and shortening. *Milk bread* is bread in which milk has been used to replace all or part of the water employed in mixing the dough. *Germ bread* is made from bolted flour mixed with germ meal or flour, containing the fatty embryo of the wheat grain, which is usually removed during the milling process to make the flour keep better. *Malted bread* is a variety made with the addition of malt extract, the diastatic power of which converts a considerable portion of the starch into sugar before the bread

is baked. *Gluten bread* contains a maximum of nitrogenous matter and a minimum of carbohydrates, and is used in the restricted dietary of diabetics. *Rye bread* may be, as it commonly is, made from a mixture of rye and wheat flours—the *Tafelbrod* or *Knüppel* of the Germans; or it may be made from straight rye flour of various grades and by different processes, as in *Pumpernickel*, *Schwarzbrod*, and *Kommisbrod*.

Rolls are small individual portions of any of the above varieties of bread. The ordinary white bread made from bolted flour is the form that will be referred to mainly; other varieties will be mentioned, when necessary, in order to illustrate some particular chemical change.

The first set of factors to be considered are the proximate chemical constituents of flour in comparison with leavened bread. The typical composition is as follows (figures in parts per hundred):

	FLOUR	YEAST-LEAVENED BREAD
Water.....	12.0	35.3
Protein.....	11.4	9.2
Fat.....	1.0	1.3
Carbohydrates.....	75.1	53.1
Ash.....	0.5	1.1

It will be noticed that the water, fat, and ash are all higher in bread than in flour. This is because water, shortening (fat), and salt are added in making the dough. The separate consideration of each of these constituents is now in order.

Water is mechanically present in all food-stuffs, from which it may be removed by processes of dehydration or desiccation without materially altering the composition of the food, though, of course, the physical properties and usually the palatability are much changed. According to some authorities, the water in stale bread is in a somewhat combined form as contrasted with the water in fresh bread. The difference is shown by the fact that the proportionate amount of water-soluble constituents is less in stale than in fresh bread from the same loaf, which can be accounted for only on the theory that the water has entered into some kind of a combination to form less soluble substances of different physical properties. The difference in the moisture content between fresh and stale bread is trifling, while the difference in physical

properties is marked. Water, in bread-making, plays more than a merely mechanical part, also, in the earlier stages of the process, where it serves as the medium for the biologic and chemical changes associated with the leavening of the dough.

Protein is the name applied to any one of a group of organic food constituents of a highly complex nature, containing the elements carbon, hydrogen, nitrogen, oxygen, and sulfur, and of vital importance as furnishing material for the construction and repair of muscular tissue, functions which no other food constituents can perform. The proteins are numerous, and are differentiated from other nitrogen-containing organic bodies by being built up structurally of units called amino-acids, of which quite a number have been isolated and analyzed. One of the best known proteins is egg-albumen (egg-white). The protein constituents of wheat flour are distinctive in not being represented at all in animal tissues and in but few other cereals. The total protein content of wheat flour is from nine to twelve per cent., which comprises the following individual proteins in approximately the following percentages, according to Osborne:

Insoluble proteins:

Gliadin.....	4.25
Glutenin.....	4.37

Soluble proteins:

Globulin.....	0.7
Albumin.....	0.4
Proteose.....	0.3

The mixture of gliadin and glutenin, which, as will be seen, are in roughly equal proportions, is known as *gluten*. It is the gluten in the flour of any cereal which gives to the dough the viscous properties which enable it to be used in making leavened bread. Wheat flour and barley flour stand highest in this respect, rye flour next (although in this case the gluten content is smaller and the doughing quality is contributed to by the development of gummy constituents of the carbohydrate group which are peculiar to rye flour), while maize flour is very inferior, and in oats and rice no gluten is found, thus accounting for the well-known fact that leavened bread cannot be made from either of these flours alone. The formation of the gluten is due to the stickiness of the gliadin binding together the insoluble and elastic particles of glutenin.

It is the tenacity of the gluten in the dough that holds the bubbles of gas introduced by the leavening process and gives "lightness" to the bread. Flours from wheats of different quality or varieties differ markedly in their dough-making qualities, and while all the causal factors are not yet known, it is believed that the elasticity of the gluten is largely dependent upon the presence and amount of certain inorganic salts, especially phosphates.

Gluten undergoes little or no chemical change in bread-making. Its peculiar physical properties give to it its particular value. The soluble proteins play a somewhat obscure and yet not unimportant part. It is believed that they have the property of modifying the gluten to a certain extent, under favorable conditions, and also that they change soluble starch into sugar. In this respect they, or some one of them probably, show enzymic properties. It is well known that if the proportion of soluble proteins exceeds a certain ratio, the flour does not make good bread.

Fat is a generic term applied principally to the glyceryl esters of fat-acids, but also to alcoholic substances, as cholesterol. The fat of flour is very small in amount (insufficient, indeed, to make good bread, so that it needs must be reinforced by the addition of lard, butter, or other shortening agent to the dough), and plays a very unimportant part in the chemistry of bread. It consists of the glyceryl esters of oleic, palmitic, and stearic acids, and a very small amount of lecithin (a phosphorus-containing fat) and of cholesterol. The fats, which are such important food constituents, as a rule are almost lacking in flour and bread, but their place is filled by the carbohydrates, which are similar in effect, though of much less proportionate nutritive value. This deficiency is also made up by the butter usually spread on bread when it is eaten.

Carbohydrate is a generic term describing an important group of organic food substances in which the essential condition of composition is the presence of carbon, hydrogen, and oxygen, the hydrogen and oxygen being in the relative proportion of two atoms of the former to one of the latter, *i. e.*, the same proportion as found in water, whence the common name, carbohydrate. Carbohydrates may be divided into two classes—the insoluble, represented in flour by starch and cellulose, which have the same empirical formula but differ markedly in their physical properties, and the soluble, represented in flour by the sugars, maltose and dextrose, and by dextrin, which has also the same

empirical formula as starch and cellulose. These carbohydrates are present in the following approximate proportions:

Starch.....	63.00 to 68.00 per cent.
Cellulose.....	2.00 to 3.00 per cent.
Dextrin.....	2.00 to 2.50 per cent.
Sugars.....	1.25 to 1.75 per cent.

Whole wheat flour contains in addition about three per cent. of lignin, a more resistant form of cellulose.

The part played by the carbohydrates of flour in the chemistry of bread-making is important. Much of the starch, it is true, is unchanged, except for the rupturing of the granules by the combined effect of heat and moisture and the production of a small amount of soluble starch by this same cause as well as by the action of enzymes. The crust or outer surface of bread consists of altered starch, and the sugars contribute to the development of the carbon dioxid or leavening gas when yeast is used. The cellulose and dextrin play a passive part, both probably remaining unchanged.

Ash.—This term includes all the inorganic constituents or salts found in foods, which are important elements in the development of bones and teeth, and indispensable to many of the vital fluids, such as blood and digestive secretions. The ash of wheat contains small amounts of all the elements commonly recognized as of essential value in nutrition; among these are potassium, sodium, calcium, magnesium and iron combined as phosphates, silicates, sulfates, and chlorids. They play but a small part of the chemical reactions of bread-making, in which they are reinforced by the sodium chlorid or salt added for seasoning. It is possible that they do play an important, if obscure, part in activating the gliadin and glutenin to form the gluten, as was previously mentioned. Their most important function, aside from this, is in supplying the yeast with some of its necessary mineral food, without which its growth would cease and the leavening power be impaired.

To these basic proximate principles of the flour used in bread-making must be added, in the special case of milk bread, the fat, proteins, carbohydrates, and salts of the added milk. While these differ slightly, the general reactions remain unaffected. Also the fat used for shortening and the sugar often used to hasten the growth of the yeast, must be kept in mind as reinforcing materials naturally found in the flour.

Having considered and described all the potential chemical factors of the

flour, it will now be in order to take up the subject of bread-making. As was previously stated, three essentially different methods of leavening, or producing lightness in the dough, are to be considered.

1. *Leavening the Dough by Aeration of a Mechanical Character.*—There are a number of ways in which this has been done. One of the earliest methods was that of Dr. Dauglish, of England. Flour is placed in a hermetically closed cylinder and exhausted of its air. Carbon dioxid is then allowed to enter, the cylinder opened, the flour removed and immediately made into a dough by the addition of soda-water (water charged to saturation with carbon dioxid, commonly called "plain soda"). The dough, while in the light and porous condition due to the bubbles of carbon dioxid entangled by the gluten, is immediately baked into loaves. In this process there is nothing added except perhaps a little salt for seasoning, and there is a minimum of change in the constituents of the flour. The changes that do occur are caused by the heat of baking, in which the starch in the interior of the loaf is gelatinized and that of the crust is dextrinized. The carbon dioxid is inert and plays a purely mechanical part, supplying the gas for distending the elastic bubbles of gluten, giving the quality of lightness to the product.

Another aeration process, somewhat similar to that described above, uses oxygen gas instead of carbon dioxid. Neither of these methods is adapted to use on a small scale. Bread has been successfully made in cold weather by mixing the flour with snow crystals, which carry enough air into the dough to give a moderate degree of aeration and consequent lightness. One of the unusual methods of aeration or vesiculation which has been proposed is to mix a small volume of strong alcohol with the dough, which is then thoroughly kneaded and placed in a warm atmosphere. The volatility of the alcohol causes it to take the form of vapor, which distends the gluten in the form of bubbles. If quickly baked, this lightness is retained long enough to set the gluten firmly, the subsequent heating driving off practically all the alcohol. Still another method, one on which a patent has recently been granted, is found in the use of hydrogen dioxid solution instead of plain water in making the dough. This is particularly applicable in bread for diabetics, the flour for which contains an extraordinary proportion of gluten, and which, by the ordinary leavening process, usually makes a tough bread. Hydrogen dioxid solution of standard strength is capable, upon decomposition, such as occurs by contact with organic matter and the heat of baking, of yielding ten times its

volume of oxygen, which provides the vesiculation so difficult to accomplish in this kind of bread.

It may be mentioned here, although it is not a part of the bread-making process, that the lightness of cakes and many other baked products is attained in a purely mechanical way by the use of white of eggs, which, being beaten to a stiff froth, entangles innumerable air-bubbles of some permanence, owing to its viscosity. This froth, when mixed with a dough or batter, carries in the necessary air to give lightness to the baked product. The rising up or puffing out of the mass during baking, which is noted in all these instances of mechanical leavening, is due to the expansion of the individual air-bubbles under the influence of the heat of the oven. It must be said that the flavor of aerated bread is markedly different from that made by either the chemical or biologic method of leavening. The absence of any foreign salts and of those by-products of fermentation which produce subtle changes in the flavor, make it more or less insipid when compared with bread made by either of the other methods mentioned.

2. *Leavening the Dough by the Employment of Chemicals.*—The chemical methods of leavening are considerably older than the mechanical methods just described. They are used because of their convenience rather than on account of their economy. None of them is at present employed on the large scale in baking bread for sale, being more frequently employed in the home for baking biscuits than for making loaf bread, although they will serve for the latter purpose also when used with knowledge developed by experience. They are all subject to the same criticism, *i. e.*, they usually leave in the baked articles products of their reaction in the shape of mineral substances not normally present in any food-stuff eaten by man in anything like the proportion in which they occur in this kind of bread.

The earliest chemical method of leavening which was developed in response to a demand for a bread not made by fermentation (yeast-bread or salt-rising bread) was used only on the large scale and consisted in the use of hydrochloric acid and sodium bicarbonate in proportions so carefully regulated that they exactly neutralized each other. The following reaction takes place:



The carbon dioxid, being in gaseous form, produces the leavening of the dough.

Theoretically, this is the least objectionable of all chemical methods of leavening, for the mineral residue left as the result of the reaction is salt, which is normally added to bread, and may as well be added in this way. The method is not suitable for use in the home, however, for it requires the services of a chemist to mix the reacting substances in the proportions needed. There is no solid compound in which the acidity of hydrochloric acid is available, as is the case with some other acids, and no baking-powder is possible giving the above reaction or one similar to it in its unobjectionable character.

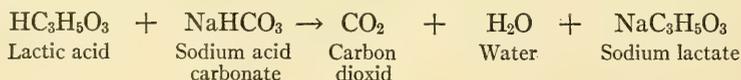
Another old form of chemical leavening agent still sometimes used by bakers, and more rarely in the home, is ammonium carbonate. Theoretically this salt is $(\text{NH}_4)_2\text{CO}_3$, which, under the influence of the heat in baking, is dissociated into $2\text{NH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}$. Practically, as found in the market, the salt is more complex, consisting of a molecule of acid ammonium carbonate (ammonium bicarbonate) and a molecule of ammonium carbamate, as follows:



This also dissociates under the heat of a baking temperature, yielding $3\text{NH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}$. In both these dissociations all the resulting products are volatile and are liberated and dissipated during the baking process, the carbon dioxide and ammonia both being gases, produce the leavening effect desired. If the product is underdone, a slight odor of ammonia is noticeable in the baked product. The commercial ammonium carbonate was so widely used at one time as to be known as "bakers' ammonia." Its disuse has been partly due to lack of skill and care to secure a product free from the objectionable odor of ammonia, and probably more largely due to the discredit which attached at one time to the ammonium salts as a class, which, before the days of their manufacture as a by-product of illuminating gas, were usually obtained from decomposing animal refuse. All ammonium salts of commerce are now obtained by the distillation of coal and are free from the above-mentioned objection.

At this same early period, before the days of so-called "baking-powders," now used so largely as leavening agents, there were two commonly used salts employed empirically to produce a chemical leavening effect. The first one of these was potassium acid carbonate (potassium bicarbonate), KHCO_3 , which, by virtue of the fact that it evolves a gas when treated with an acid, was called "sal aëratum," usually shortened to "saleratum." Later the

potassium salt was replaced by that of sodium, NaHCO_3 , which was called "soda saleratus," and is now extensively used under the name of "baking soda." This compound (and also its predecessor, the potassium salt) was at first employed and is still used in all homes, with certain acid liquids used in the preparation of the dough. These acid liquids are molasses, used in the preparation of cake but not of bread, and sour milk, used in cakes, biscuits, or bread. Cream of tartar is also used in the kitchen as a factor for decomposing baking soda and will be referred to under the baking-powder containing it. The acids of molasses are the natural acids of the sugar-cane juice plus a small amount resulting from alteration during its handling. There being no single predominating acid, it is not possible to write a simple reaction for the decomposition of sodium bicarbonate by molasses. Whatever acids there are yield the carbon dioxide by a decomposition analogous to any of those given below. The acid of sour milk is lactic acid, which has the empirical formula $\text{HC}_3\text{H}_5\text{O}_3$. The reaction between this and sodium acid carbonate is:



The leavening effect is produced by the carbon dioxide. The sodium lactate resulting from the reaction remains in the baked product in greater or lesser amount, depending upon the acidity of the milk and the amount of sodium bicarbonate which has been used. The lactic acid of sour milk, like the hydrochloric acid previously referred to, does not exist in any solid form of stable character, and is, therefore, not available for use in a baking-powder.

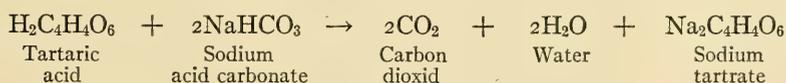
In the empirical or home use of saleratus or baking soda as a leavening agent with decomposing factors of doubtful or varying acidity, as have been described, it sometimes results that the alkaline compound is present in slight excess. When this is the case, the baked product possesses what is called a "soda taste," disagreeable to most persons and which is due to the decomposing influence of heat and moisture upon the sodium acid carbonate, converting it into sodium carbonate according to the following reaction:



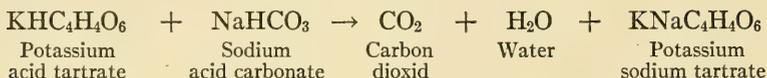
This condition never occurs with manufactured baking-powder, as the ingredients are so calculated as to produce exact neutralization or leave a slight trace of the acidic element.

The early discovery of acid potassium tartrate (potassium acid tartrate), commonly called "cream of tartar," in grape-juice and its economic production as a by-product in wine-making, was due to the fact that it is less soluble in alcoholic than in aqueous liquids and separates out during the fermentation of the must as a crystalline deposit. The crude substance is known commercially as argol. It was at first, and is still, often used empirically with one of the forms of saleratus to produce a leavening effect. The fact that it occurs in a solid form of great purity and marked permanence led to its early use in a mixture with sodium bicarbonate to produce what is commonly called baking-powder. Baking-powders are more largely used in preparing cakes or biscuit than for the preparation of loaf bread, although it is quite possible to use them for such purpose. They are of three well-known types. First, the tartrate powders, in which cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$, or tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, serves as the acidic element. Second, the phosphate powders, in which calcium acid phosphate, $\text{CaH}_4(\text{PO}_4)_2$, or sodium acid phosphate, NaH_2PO_4 , is used for this purpose. Third, those in which compounds of aluminum, as common alum (aluminum and potassium sulfate, $[\text{K}_2\text{Al}_2(\text{SO}_4)_4]$), ammonium alum (aluminum and ammonium sulfate, $(\text{NH}_4)_2\text{Al}_2(\text{SO}_4)_4$), or sodium alum (aluminum and sodium sulfate, $\text{Na}_2\text{Al}_2(\text{SO}_4)_4$), are employed to liberate the carbon dioxid from the sodium carbonate. In all these, sodium acid carbonate is used as the gas-liberating constituent because it is lower in price than the potassium salt and also because it liberates more gas than an equal weight of the potassium salt. There is also a large proportion of inert or diluting material, usually corn-starch, wheat flour or some other absorbent material, added for the purpose of keeping the acidic and gas-liberating ingredients mechanically separated, for if these come into close contact in the presence of even minute proportions of moisture, as are always absorbed by substances kept in any but hermetically sealed containers, the reaction slowly proceeds, and when the powder is to be used, it might not have any leavening power, because the gas would have already disappeared. In some few powders magnesium carbonate is used, partly as a moisture absorbent and partly for its carbon dioxid yielding properties. In the tartrate powders the reactions are as follows:

When tartaric acid is used:



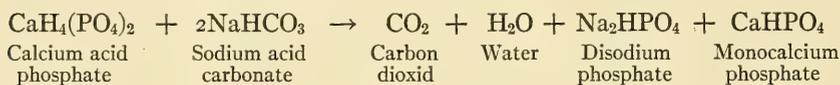
When cream of tartar (potassium acid tartrate) is used:



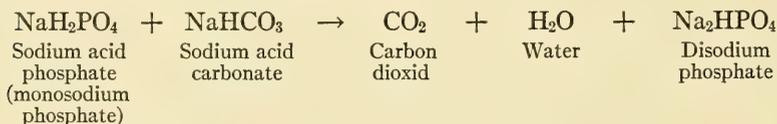
The residue in the first case is sodium tartrate and in the second potassium and sodium tartrate, better known as Rochelle salt or Seignette salt. Both of these salts are purgative in their action and remain in the bread or biscuit as substances not normally in the human body nor of any especial use to it. The amount of Rochelle salt left in food made with a cream of tartar baking-powder is almost exactly equivalent in weight to the amount of baking-powder originally used, as the Rochelle salt crystallizes with four molecules of water of crystallization, which largely increases its weight.

In the phosphate baking-powders the reactions are as follows:

When acid calcium phosphate is used:

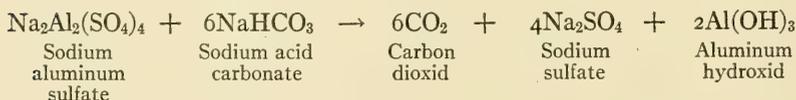
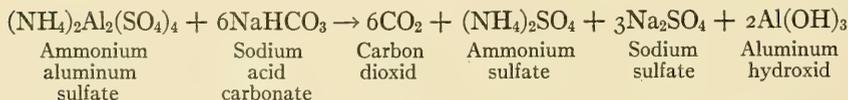
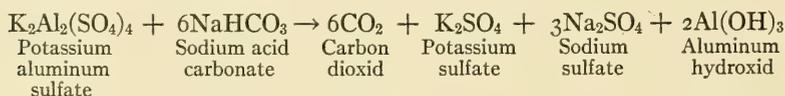


When acid sodium phosphate is used:



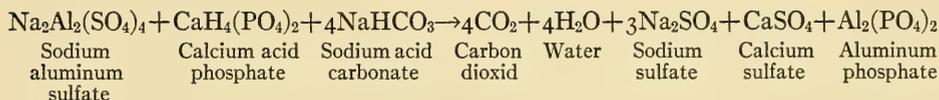
The residue in the first case is a mixture of disodium phosphate and monocalcium phosphate. The monocalcium phosphate is an insoluble salt which passes through the alimentary tract mostly unchanged. The disodium phosphate, which is the sole fixed residue of the second reaction, and is also present in the first reaction, is the soluble salt commonly known and used as a cathartic under the name of sodium phosphate. The amount of this salt is only a little more than half of the original weight of baking-powder taken.

In the alum powders the reactions are as follows:



When these powders are properly made, no alum remains after the leavening reaction, though by misleading advertisements by firms making other types of powders, many persons are led to believe the contrary. There remain, however, in the food, as foreign substances, insoluble aluminum hydroxid and the soluble sodium sulfate; the latter, commonly known as Glauber's salt, used as a cathartic, particularly in veterinary practice. Soluble ammonium and potassium sulfates remain in the food made from those alums respectively.

A modification of alum powder has been manufactured which contains a mixture of one of the alums and monocalcic phosphate. The reaction in this case is somewhat different, and with the sodium alum (the one most commonly used in alum powders, as it is the cheapest and is known to the baking-powder trade simply as "S. A. S.," which is an abbreviation of its chemical name, sodium aluminum sulfate) is as follows:



In this case the insoluble residue is aluminum phosphate, while the other salts are the soluble sodium sulfate and the difficultly soluble calcium sulfate.

As may be readily appreciated by any person of intelligence and discernment, all the chemical leavening agents reactions of which have just been described are open to the same objection, *i. e.*, that a foreign salt is formed in the food in which they are used. It, therefore, is merely a question of which is the least objectionable. The choice in this respect lies closely between the phosphate and tartrate powders, with the combined alum and phosphate powder next and the alum powders last. Any of them might be harmful if eaten every day.

3. *Leavening the Dough by the Use of Yeast.*—Yeast is a unicellular organism of minute size (about $\frac{1}{4000}$ of an inch in diameter), belonging to the vegetable kingdom. Many species have been identified, only a few of which are of value in bread-making. That most frequently employed is *Saccharomyces cerevisiæ* (literally, the sugar fungus of beer). Each individual yeast cell is capable of reproduction and requires nourishment for its growth and multiplication during which it exercises the functions that make it valuable in bringing about fermentation. Yeast requires a variety of nutrients, just as

other organisms of a higher type. Carbohydrates, protein and mineral salts are all essential. Just as certain constituents are necessary in soil to support plant life, so are certain constituents needed in any medium supporting yeast in order to develop the maximum efficiency. In the empiric method of using yeast, which has been followed until very recently, it was a matter of accident and not of intent whether several of these constituents were present, and it is now easy to understand why bakers in certain localities would get better results on account of the presence of certain constituents in the water used in the preparation of the dough. Studies have recently been made of this subject from the standpoint of scientific research, and Dr. Kohman, of the Mellon Institute of Industrial Research, Pittsburgh, Pa., has recently contributed some valuable facts to our knowledge of the subject.

Among the mineral substances found to be of value are calcium chlorid, ammonium chlorid, calcium sulfate, ammonium sulfate, and potassium bromate.

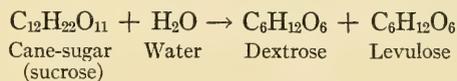
Certain proportions of these salts bring about a great increase in volume of carbon dioxide in a given time, which is of value in enabling less yeast to be used and also in shortening the time of fermentation. Other advantages are lower consumption of sugar and better quality of the bread. All of the foregoing substances but the potassium bromate are found usually in some amount in natural waters and in other ingredients in common use. The potassium bromate is a salt entirely foreign to any natural source and was employed in the experiments because it is an oxidizing agent. It was found to have remarkable properties as a yeast stimulant, even when used in so small a proportion as one ounce of the bromate to 10,000 loaves of bread. This would leave such a small proportion of its decomposition product (potassium bromid) that a person would have to eat a whole loaf of bread each day for several years to obtain the average medicinal dose of the salt.

The results of some of these researches and investigations have leaked out through the newspapers occasionally in a distorted and exaggerated form, usually in the shape of allegations that the bakers are adding plaster-of-Paris, sal ammoniac, etc., to their bread, and giving the impression that these are used as adulterants or in large amounts, or in some other reprehensible manner. The scientific and careful use of such chemicals as yeast foods is not only proper and commendable, but should be encouraged in the interests of economy and public welfare, as they tend in every way to improve quality and diminish cost.

Among the nitrogenous constituents of value as yeast food is *asparagin*, a moderately widespread plant principle, found in largest amount in asparagus, whence it gets its name. This principle exists in small amount in potato but not in the cereals, which may account for the empiric use of potato water in preference to other liquids in making yeast extemporaneously, as is sometimes done in the home.

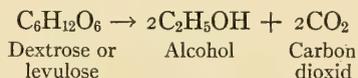
It was at one time believed that yeast and other organized ferments, as they were called, acted in a manner essentially different from the enzymes or unorganized ferments. This view is now known to be erroneous, and it has been proved that yeast acts through the agency of enzymes secreted during its life and growth.

Yeast breathes or takes in oxygen and exhales or gives off carbon dioxid when surrounded by a favorable medium for its activity. The soluble carbohydrates constitute the food element needed in largest amount for the exercise of its functions. If the sugar is present as a disaccharid, such as cane-sugar, known as an indirectly fermentable sugar, it is necessary first for one of the yeast enzymes (the one named invertase) to transform the disaccharid into the directly fermentable monosaccharid, which it does by the following reaction. This reaction, as will be seen, is one of hydrolysis, in which the enzyme plays no part that can be expressed:



The dextrose and levulose of the foregoing reaction are isomeric sugars differing in their optical activity, and the mixture is known as invert sugar.

Having a monosaccharid at its disposal, and assuming that it has been provided with proper nourishment, the yeast acts upon the sugar and produces alcohol and carbon dioxid, according to the following reaction:



The carbon dioxid produces the leavening effect; the alcohol is mostly driven off by the baking, so that in freshly baked bread the proportion is rarely above 0.25 per cent., and this rapidly diminishes to zero after the loaf is cut. As may be readily appreciated, yeast works more actively at some temperatures than at others. Too great activity is not desirable, for abnormal

fermentations result in the production of larger amounts than usual of certain by-products of yeast action, such as glycerol, succinic acid and some of the higher alcohols, such as amylic, to which bread that has been leavened with yeast may owe its distinctive flavor. The optimum or most favorable temperature at which yeast works ranges from 86° to 89° F. (about 30° to 32° C.). Marked deviations from this temperature bring about changes in which the quality and flavor of the bread are appreciably altered. Through carelessness in respect to the temperature, other fermentations, such as the acetic or lactic, may develop and the resulting product be ruined. For many centuries much yeast-leavened bread was made empirically by developing home-made cultures of wild yeasts by spontaneous inoculation and generation in starchy culture-media, particularly the potato, to which reference has been made above. Sometimes instead of exposing to accidental infection from the air, these culture-media were inoculated from previous cultures left over or borrowed. Such empiric and irregular methods were not conducive to uniformity in the resulting bread, and bread-baking has progressed more during the few years since commercial yeasts are available than it did for centuries previously. The commercial yeasts are usually sold in the compressed form, made by growing carefully selected strains of pure yeast in properly made nutrient media and subsequently removing the excess of moisture and mixing with a certain proportion of starch which acts as an absorbent.

When alcohol is the desired object of the fermentation, large amounts of sugar are needed during the process. As in the case of bread-making, it is the carbon dioxid that is sought, and as a gram of sugar is capable of yielding 8.2 c.c. of carbon dioxid, it is a fact that the sugar naturally present in wheat flour, while present only to the extent of from 1 to 1.5 per cent., is amply sufficient to supply the yeast for the maximum leavening effect desired. It is usually the practice, however, to add a little sugar, which has the effect of hastening the operation. Even if no sugar is added during the making of the bread, the dough usually shows a higher proportion of sugar after fermentation than before, notwithstanding the use of it by the yeast. This is due to the fact that when water is added to flour it develops the enzymic reaction of the flour and some of these naturally occurring enzymes are capable of transforming a small proportion of the starch in the flour into soluble carbohydrates or sugars.

During fermentation there is a loss of from one to three per cent. of the total protein of the flour used by the yeast as food. The acidity of bread,

which amounts to a small fraction of one per cent., as a rule, is due to lactic acid with small traces of acetic acid (about ninety-five per cent. lactic and five per cent. acetic); sometimes, but rarely, butyric acid is present if improper fermentations have set in.

4. *Leavening the Dough by the Action of Bacteria.*—For many years one of the home methods of making leavened bread practised in many localities was the “salt-rising” process, as it was usually called. In this method of bread-making wheat flour and corn meal are mixed with hot milk and salt and set in a warm place. In the course of a few hours fermentation sets in and the whole mass becomes porous. In this condition it is mixed with flour to make a dough, as in the slack sponge process of wheat-bread making. This dough, when set aside in a warm place, undergoes a fermentation similar in many respects to that produced by yeast. The underlying principles of this method were not clearly understood until very recently. Even as late as 1898 the United States Department of Agriculture, in an official publication, stated, regarding this process, that “the fermentation of dough may be secured by enzymes naturally present in flour.”

It has been shown by research work on the subject that the above changes are due to bacteria of certain types. Pure cultures of these bacteria are now furnished for use on the large scale for this method of bread-making. The chemical reactions have not yet been studied sufficiently to be intelligently described. It is known that no alcohol is produced during the decomposition changes and that carbon dioxide and hydrogen are the gases to which the leavening effect is due. The bacteria act upon the sugar of the flour and upon the sugar and the casein of the milk used in the initial stages of the process.

Chemical Changes During Baking.—The temperature at which bread is baked ranges from 180° C. (355° F.) to 220° C. (425° F.). The changes produced by the heat are not as numerous nor as marked as might be supposed. The major portion of the starch, which is the most abundant constituent of bread, is not affected chemically, but is altered physically by the combined effects of heat and moisture, so that the individual granules are greatly distended or entirely ruptured. A small proportion of soluble starch is produced by the heat in the interior of the loaf, while the exterior of the loaf has had a large proportion of the starch converted into the isomeric substance dextrin, $C_6H_{10}O_5$, from the same cause. It is this constituent which gives the sweet taste to the crust. After baking, the principal change which occurs is the

diminution of the water (drying out) and the retention of part of the water in the peculiar form spoken of under water as a constituent of bread.

Sometimes changes of an abnormal character occur, usually of biologic origin, caused by molds, bacteria, etc., as noticed in ordinarily moldy bread in which the common mold gives a green color superficially. A red bread is sometimes seen, caused by a less common microbe. This being of a bright color resembling blood, is startling when seen for the first time, even by an educated person who knows how to account for it. Among the ignorant it usually causes unwarranted fears, hard to allay. Ropy bread is another condition of abnormality brought about by bacterial action. In such bread, when pulled apart, the crumb, instead of breaking off more or less short, stretches out into long elastic strings. These conditions are all accompanied by chemical changes, imperfectly understood, and not capable of definite description.

In wrapped bread, now coming into more wide-spread use in response to the modern demand for more careful sanitary handling of foods, there are also some more or less obscure changes likely to occur, especially if it is wrapped in absolutely impervious paper, which has come to be recognized as not so good as one which is slightly porous. Moldiness and souring have been reported. Increase in the amount of aqueous extract, partial hydrolysis of starch, increase in amount of soluble proteins, and increase in acidity have all been reported. These changes are all undoubtedly due to the action of molds or bacteria. They are being studied constantly, and as our knowledge increases these changes are being minimized by knowing just the length of time the bread must stand before being wrapped as well as the proper kind of paper to use in wrapping. If, however, these precautions are observed, wrapped bread is just as good and wholesome as unwrapped bread.

The foregoing chemical changes are those normally occurring in bread-making. It is proper, in closing, to refer to some of the adulterants of bread and the chemical changes, if any, resulting from their use. Such adulterants as talc, terra alba, clays, etc., which have been reported in former times, are purely mechanical and play no part in the chemistry of the subject. Their presence has not been reported for many years, and they are of little or no importance at present.

Potassium alum has been used surreptitiously during several hundred years for ostensibly improving the bread, but is now forbidden by the food

laws of most countries and is rarely met as an adulterant of bread. It had the effect, when added in the proportion of one-half lb. to 380 lbs. of flour, of making the bread white, and also preventing the loaves, which come in contact with each other in the oven, from sticking together and pieces being pulled out when the loaves are separated. The reason for these effects has never been ascertained. The use of alum was so prevalent at one time that it was popularly known in bakeshops by such names as "stuff" and "rocky," for the purpose of concealing its identity. As, in order to be of any value, it was needed in the proportion of from three to five grains to each loaf of bread, and as the tests for detecting it are comparatively simple and the penalties for its use very severe, it is rarely found now.

Copper sulfate (blue vitriol) is another substance that has been clandestinely used as a bread improver. In proportion of one grain to the loaf of bread, it whitens and improves the appearance of bread, even when baked from inferior and dark flour. It, too, is readily detected, and with the severe legislation against its use, it has disappeared.

In the case of both alum and copper sulfate the effect is probably due to the retarding influence they have upon the enzymes of flour, as it is well known that in damaged and inferior flours the enzymes are present in abnormal amounts.

Magnesium carbonate and calcium carbonate, chalk, have also been used as flour improvers in the proportion of from twenty to forty grains of the substance to each pound of flour. Their effect is similar to that of lime-water, sometimes mixed with the water used in making the dough. They are all used in improving or restoring damaged flour, which they probably do by neutralizing the acidity frequently present in such flour and also by retarding the enzymic action just referred to under alum and copper sulfate, as in this enzymic action the starch is hydrolyzed to sugar and the gluten decomposed to a certain extent, and any retardation of this change, when abnormal, would increase the water-holding power of the flour and improve the appearance and texture of the loaf.

Bleached flour also contributes its quota to the chemistry of the subject. Flour is industrially bleached by exposing it to the action of chlorine, ozone, nitrogen oxides or nitrosyl chloride. The most marked changes occur in one of the minor constituents of the flour, the fat, which forms combinations with several of the bleaching agents, of greater or less permanence, which serve for fixing the bleaching agent for identification later.

CATALYSIS IN THE INORGANIC FIELD

DAVID WILBUR HORN

Delivered April 24, 1917

CONTACT underlies chemistry. While bodies influence each other at almost incredible distances, as is shown in the mutual influence of the earth and the sun through a distance of about 92,000,000 miles, this action is physical, not chemical. Briefly, no contact, no *chemical* action.

An attempt to refine the idea of contact leads to the conclusion that contact may be as intimate as the fineness and structure of matter will permit. Undoubtedly better contact is possible between bird-shot than between cannon-balls. And if contraction and interpenetration occur, better contact would be realized than would be possible between incompressible and impenetrable bodies.

Such speculations are, however, scarcely warranted. These are the days when the structure of the atom is in doubt, as it has, of course, always been, and when the doubt is generally admitted; and it is wiser not to venture far beyond experiment in speculations on energy and matter. Further, the object of the present lecture is narrative and descriptive.

Contact may conceivably be a process involving only two substances, but this conception is seldom realized in practice. Even when two pure substances are obtainable (if ever) we are likely to confront the problem of excluding the all-pervading atmosphere with its several constituents and different foreign bodies. When minimizing this source of complications by working in the erroneously named "vacuum," our two pure substances would still be affected by the presence of matter in quantities demonstrably capable of profound effects, as the work in radio-active phenomena and in physiologic chemistry shows. In any enclosed system the walls of the containing vessel are always a part of the system and, as will be seen later, may influence chemical changes radically.

The foreign bodies present at contact of two substances may, of course, be inert or active. In by far the larger number of cases studied in the development of chemical knowledge the foreign body was inert or its action escaped attention, therefore, the time-honored generalizations of chemistry, its "fundamental laws," refer to the action of pure substances upon each other without reference to the effects of adjacent bodies.

In some few instances, however, the effects of adjacent bodies were so striking as to compel early attention. Until recent years, the multiplication of such instances has been slow. Such action or influence of an adjacent body may be covered by the word "catalysis," introduced by Berzelius in 1834. The influence of the adjacent body, like the influence of the main substances in a reaction, is profoundly affected by the state of subdivision of the adjacent body. When potassium chlorate is heated in a silica test-tube, for example, the decomposition occurs at an elevated temperature and irregularly. If finely ground silica is first mixed with the chlorate, the chlorate decomposes more rapidly and more oxygen is obtained in a given time without heating to as high a temperature.

Although contact and a state of fine subdivision favor "catalysis," they are not the most fundamental requirements. These most fundamental requirements are the problem of today. Apparently, the *nature* of the adjacent body is capable of exerting the preponderating influence. In catalysis, the adjacent body merely alters the rate of a reaction that also occurs of itself, and in so doing the catalyst does not increase or decrease in amount. Most known catalysts accelerate changes; some retard changes and are called "negative catalysts."

It is important to answer the question why substances may be brought into intimate contact without noticeable chemical action resulting. Two answers may be given: (1) The two bodies may have little or no chemical attraction or affinity for each other, as, for example, fluorine and oxygen. (2) The two bodies may have an affinity for each other but the rate at which they react may be too slow to produce noticeable amounts of product in the period of observation.

In the first instance, no catalyst could have any effect. Only in the second instance could catalysis occur. The reason for this statement lies in the laws of energy. Mechanical (or available) energy can never spontaneously increase. It is clear that if catalysts could cause reactions otherwise impossible because no chemical affinity existed between the two bodies in contact, we might, by a suitable selection of catalysts, arrange cyclic chemical processes that would continue to supply available energy so long as energy of any kind remained in the system. But experience has taught that the molecular motions and strains that constitute thermal energy cannot be so treated by the aid of catalysts, or by any other aid whatsoever.

Historically, catalysis is not a new phenomenon. Processes of fermentation were known to the ancients, and these involve catalysts. In fermentation

by yeast, the yeast plant produces the catalyst, or enzym, as it is more frequently called. The Arabs are said to have known the catalytic action of sulfuric acid in the conversion of alcohol into ether. The alchemists knew that niter hastens the purification of gold by cupellation, and that sulfur will produce sulfuric acid if saltpeter is first mixed with it. Otherwise, sulfur burns mainly to sulfur dioxid.

In 1836 Berzelius, the famous Swedish chemist, compiled all cases known in which, by the presence of a foreign body, a chemical reaction is hastened without the foreign body itself being changed. These foreign bodies thus acting Berzelius named "catalysts." This classification included all those actions that Mitscherlich had discussed but a short time before. In dealing with the process of making ether from alcohol Mitscherlich named the sulfuric acid a "contact substance," expressing thus the thought that the sulfuric acid was active merely and solely by its presence and its contact. A recent definition of a catalyst or contact substance includes substances that affect the velocity of a chemical reaction without appearing in the final products.

In sharp contrast with chemical reactions that, when not catalyzed, proceed at so low a rate as to produce less than noticeable amounts of products, stand the reactions that are so rapid as to be practically instantaneous. Reactions between ions are, for example, practically instantaneous. Of course, catalysis is not concerned with such reactions.

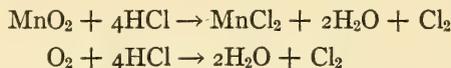
It is not strictly true that a catalyst is found to be *unchanged* at the end of a catalyzed reaction. It is correct to say that the final products are the same as they would have been had the catalyst been absent. The catalyst may be rather unmistakably changed, not in amount but in physical state. Thus the crystalline manganese dioxid used to generate oxygen from potassium chlorate becomes a fine powder, and changes in physical state are known to occur in iron oxid and in platinum used as catalysts in other systems. The amount of the catalyst, no matter how small, seems to remain unchanged. Catalysts themselves may be accelerated or restrained in their rapidity of action. Two catalysts usually have a greater joint effect than either would have singly. "Promoters" that increase the activity of catalysts are also known. Some substances so completely obstruct the action of catalysts that they have been called "poisons." Enzymes and toxins have their poisons and antitoxins, and the analogy to them is quite close, even in the case of metallic catalysts.

Some catalysts seem specific for a given reaction, but many catalysts are

capable of manifold application. No general method for guidance in selecting a catalyst for a given reaction is known.

Confining ourselves strictly to the subject assigned to us tonight,—“Catalysis in the Inorganic Field,”—three great processes of chemical industries demand attention. All three involve the use of that great reservoir of raw material, the atmosphere.

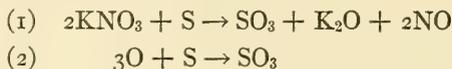
The first, Deacon’s process, is the most successful method for producing chlorin without the use of a manganese compound. It is well to compare the non-catalytic process with Deacon’s process, by aid of equations:



The catalyst is cupric chlorid at 400° , used on pumice, broken brick or other porous refractory material as a support. Numerous other substances catalyze this change, less effectively, however, than cupric chlorid; for instance, ferric chlorid, platinum, chromic oxid, nickel chlorid.

To poisons, cupric chlorid is one of the most sensitive catalysts. Arsenous and arsenic oxids and sulfur trioxid must be removed from the gases, as well as all moisture. Temperatures above 460° cause the catalyst to volatilize too rapidly, and temperatures below 400° give too low a yield. The “decomposers,” therefore, as the chambers that contain the catalyst are called, are built in separate compartments each of which may be emptied and recharged without discontinuing the flow of gas through the others.

The second of the great chemical industrial processes for consideration is the manufacture of sulfuric acid. Sulfuric acid is probably the most important of all chemicals, because of its extensive use in numerous manufacturing processes. In 1740 Ward began manufacturing this acid, in England, by burning sulfur and niter together and condensing the vapors in glass vessels containing water. These were soon replaced by lead vessels, and later steam was introduced instead of water, and nitrogen oxids prepared by the decomposition of niter in a separate vessel and air were also introduced. For comparison, the reactions in these two processes may be written:



although it is well known that neither reaction is as simple as represented in these equations. They serve, however, to emphasize the greater simplicity

assumed for the catalytic process (the leaden-chamber process) in which the nitrogen oxids act as catalyst.

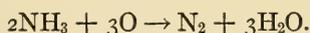
A second catalytic process for the manufacture of sulfuric acid uses platinum as catalyst. Careful temperature control is one of the most important factors, and the operation is conducted at about 420° . The enormous heat evolution in the reaction is controlled by using it to pre-heat the mixture of sulfur dioxid and air before it reaches the asbestos or other substance on which the catalyst, platinum, is supported.

Arsenic and suspended impurities soon "poison" the catalyst. To prepare the mixed gases, therefore, they are carefully cleaned with steam, then washed, and then passed through sulfuric acid of such strength as to remove all but that amount of water-vapor needed for the reaction to take place.

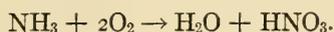
Less expensive catalysts in large number have been tried, of which ferric oxid as pyrites-cinders is probably the only one used commercially. Since it operates best at a higher temperature and even then has a lower efficiency, it may be used satisfactorily along with platinum. The hot gases are first passed over the iron oxid catalyst and later over the platinum. The sulfur trioxid formed is absorbed in dilute sulfuric acid.

The third of the great industrial enterprises that rest upon catalysis is the obtaining of certain nitrogen compounds by use of the nitrogen of the air. Nitric acid is perhaps the most important, and its production is a national necessity. It is officially estimated that the United States would need 180,000 tons per annum when at war with any first-class power. It is hazardous to rely, in war, upon the sodium nitrate deposits of Chile, or upon the waterfalls that lie upon the border of the nation with which we have more frequently quarreled than with any other—the British Empire. Niagara furnishes electric power at a cost sufficiently low to permit its use in manufacturing nitric acid by the method of passing air through a properly constructed electric arc, but the cost at its lowest is high, and only a part of the waterpower of Niagara is ours.

By burning ammonia, nitric acid may be produced, although ordinarily the change is represented by the equation:



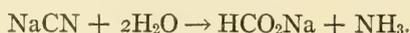
When platinum is present, under proper conditions, the rate of another reaction may be sufficiently changed to make it the principal reaction, namely,



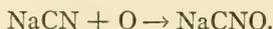
This is accomplished by passing a proper mixture of air and ammonia rapidly through a plug of smooth platinum coated with spongy platinum. The proper temperature for the catalysis is obtained by heating the gases before entry at the expense of the gases issuing from the region of catalysis. Other catalysts for this process are known, but platinum has been most used. This process makes the production of nitric acid directly dependent upon the production of ammonia. As sources of ammonia we have the gas and coke plants, in which coal is destructively distilled; the later processes in which nitrogen from the air is made to combine with elements to form, for example, nitrids, or with compounds to form, for example, cyanamids, from which ammonia is directly obtainable; and lastly, the direct union of nitrogen from the air with hydrogen.

This last-mentioned process involves the use of pure iron as a catalyst, judging from the data obtainable; but other metals have also been found to have more or less catalytic action under similar conditions. A highly developed form of special apparatus is required (shown and explained by lantern-slide) in which the gaseous mixture or the separate gases may be raised to 650°–700° C. while under 200 atmospheres pressure. The “poisons” to the catalyst in this process are numerous and difficult to remove. (See page 12.)

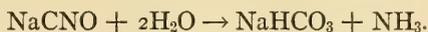
The disadvantages of the high cost of electric current, the unfortunate location of our best hydroelectric plants, the difficulties of highly developed forms of special apparatus, the ready poisoning of most catalysts, the necessity for highly purified gases—all these and other disadvantages have been overcome in a method for the fixation of atmospheric nitrogen now (March) current in our chemical journals. I refer to Bucher’s process, in which air is passed over heated coal or coke previously mixed with an alkali, and with finely divided iron which acts as the catalyst. An alkali cyanid results. The catalyst operates at a moderate temperature, 900°–950°, and could be installed in an emergency almost anywhere. The process means something more than a mere addition to our fighting power, for it can serve to increase our agricultural resources enormously. The sodium cyanid produced, if soda is the alkali used, is readily convertible into ammonia and sodium formate:



If the cyanid is kept just above its melting point and a current of air passed through it, it burns to sodium cyanate:

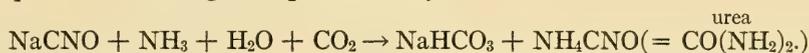


One-half of the cyanate is now heated with water, which converts it into ammonia long before the boiling point is reached, according to the equation,



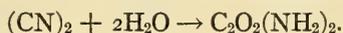
The sodium acid carbonate is thrown back into the process, and the ammonia later converted into *urea* as follows:

The other half of the sodium cyanate is added to water and the ammonia passed in. Then carbon dioxide from the cyanizing furnaces is also passed into the liquid. The change is represented by



This is "a very inexpensive way of getting urea, which has over 46 per cent. of nitrogen"—much more than our common and excellent fertilizers, ammonium nitrate and ammonium sulfate.

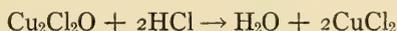
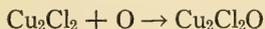
If cyanogen gas (obtained from some of the sodium cyanid) is passed into 44 per cent. hydrochloric acid, it is hydrolyzed readily to oxamid:



Oxamid has nearly 32 per cent. of nitrogen, is nearly insoluble in water and should be especially of value as a fertilizer.

Nothing short of a careful study of Dr. Bucher's article can convey a proper conception of its great possibilities and its vital importance to our nation.

The mode of action of catalysts is open to debate. Undoubtedly in many instances intermediate compounds between the catalysts and one or more of the reacting substances are formed. These intermediate compounds subsequently break down to form one of the products of the chemical change and to regenerate the catalyst. The action of the cupric chlorid in Deacon's process has been explained by some by means of these equations:



In the lead chamber process, under certain conditions, an intermediate compound crystallizes out. This compound has been used in explanation of the catalytic action of the nitrogen oxid as follows:



or



Other analogous instances of intermediate compounds in catalytic changes might be cited, but after all there would remain quite a number of such changes not readily accounted for in this way. The method of catalytic action is an open question, which for its solution will require time, experience, and careful investigation.

The following experiments were performed in the course of the lecture:

1. To illustrate negative catalysis, illuminating gas containing ethylene was mixed with air and passed into a Hempel phosphorus pipet. No oxidizing action on the phosphorus was indicated, either by phosphorescence or fumes. The gas-mixture was then transferred to an absorption pipet containing bromin-water to remove the ethylene, after which it was once more passed over the phosphorus, when fumes and phosphorescence became at once marked. According to Winkler, minute amounts of ethylene act in this way as negative catalyst, preventing the oxidation of the phosphorus.

2. A thin platinum dish was held over a bunsen flame until red hot, the flame was then extinguished, but the gas allowed to flow. The dish continued to glow, because the gas burned, without flame, in contact with the platinum.

3. Hydrogen peroxid solution (3%) was poured onto manganese dioxid; gas was rapidly evolved by the catalytic action of the dioxid, and being tested with glowing splinter of wood was shown to be oxygen.

4. A dilute solution of potassium iodid was acidified with acetic acid, treated with hydrogen peroxid solution and starch paste, and the mixture divided into two portions. To one of these, ferrous sulfate was added. The characteristic starch-iodin reaction appeared at once in this portion, because the ferrous salt acted as a catalyst. The other portion very slowly developed the blue.

5. A dilute, cold mixture of solutions of oxalic acid and potassium permanganate was divided into two portions. To one a small amount of manganous sulfate was added; the color of the liquid was promptly discharged by reason of the decomposition of the permanganate, while it persisted for a long while in the portion to which no manganous salt had been added.

The following lantern slides were shown in the course of the lecture:

1. Diagram of a complete plant for Deacon's process.
2. Diagram of details of construction of "decomposers" in Deacon's process.
3. Diagram of a complete lead chamber plant for manufacture of sulfuric acid.
4. Diagram of details of the lead chamber and its immediate attachments.
5. Diagram of a complete contact plant for sulfuric acid.
6. Diagram of the details of the contact apparatus.
7. Diagram of the Haber apparatus for the catalytic process of making ammonia from hydrogen and nitrogen. (See page 12.)

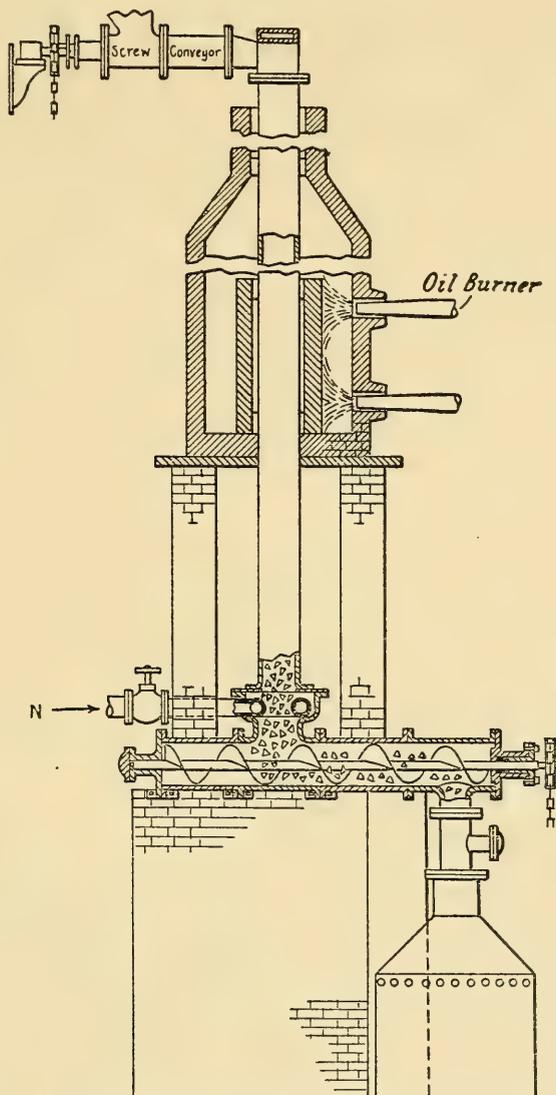


Fig. 1. (Courtesy of *Journal of Industrial and Engineering Chemistry*.)

8. Diagram of Bucher's apparatus for making sodium cyanid (Fig. 1), with the charge continuously moving. This apparatus is designed "to keep the final concentration of alkali in the briquets just the same as at the beginning, because whatever distilled from the heat-zone, would have to return to it."

9. Diagram of Bucher's apparatus for the use of air or producer gas in place of pure nitrogen (Fig. 2). Several inches of layers of coke were held in position in the tube with iron screens, and another screen kept the briquets away from the porous absorbing surface of the coke. The (iron) pipe was heated to the cyanizing tempera-

ture, and a current of air passed in. When the process was over the air was shut off before the tube was cooled.

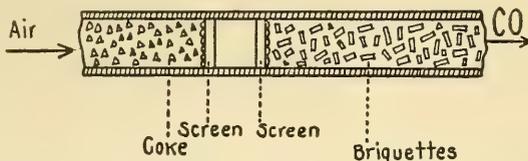


Fig. 2. (Courtesy of *Journal of Industrial and Engineering Chemistry*.)

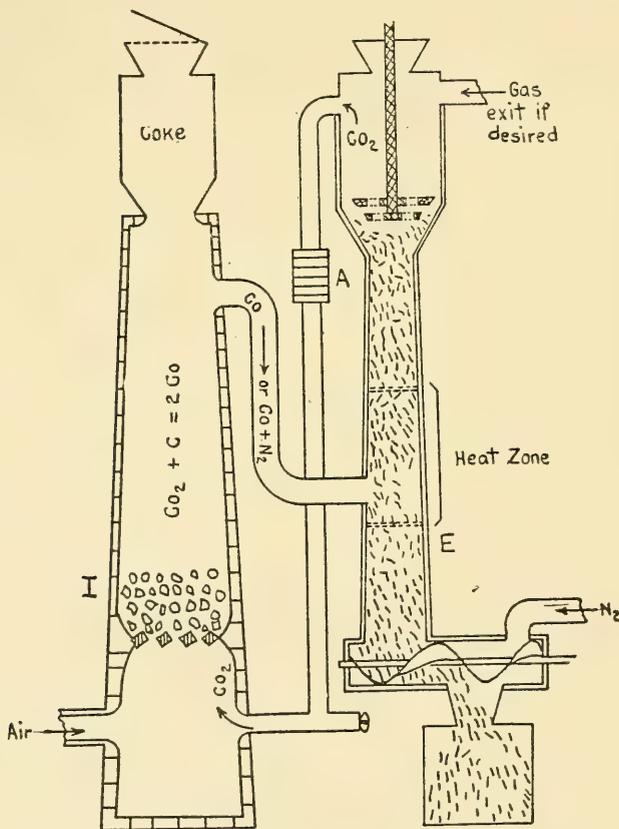


Fig. 3. (Courtesy of *Journal of Industrial and Engineering Chemistry*.)

10. Diagram of Bucher's "continuous furnace" (Fig. 3), to avoid the destructive effects of cooling the briquets in producer gas. By simply passing the producer gas into the briquet column at the base of the heat-zone, the cyanized briquets are entirely away from the producer gas. The arrangement is such that either nitrogen or producer gas may be used.

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