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A field gun arranged for high-angle fire.

REPELLING ATTACKS OF AIRCRAFT.—[See page 30.]

Physiological Importance of Phase Boundaries*

A Consideration of the Physical and Chemical Systems Concerned in Living Cells

By Prof. W. M. Bayliss

EVEN a hasty consideration of the arrangements present in living cells is sufficient to bring conviction that the physical and chemical systems concerned operate under conditions very different from those of reactions taking place between substances in true solution. We become aware of the fact that there are numerous constituents of the cell which do not mix with one another. In other words, the cell system is one of many "phases," to use the expression introduced by Willard Gibbs.

Further, parts of this system which appear homogeneous under the ordinary microscope are shown by the ultra-microscope to be themselves heterogeneous. These are in what is known as the colloidal state. Some dispute has taken place as to whether this state is properly to be called a heterogeneous one, but it is sufficient for our purpose to note that investigation shows that the interfaces of contact between the components of such systems are the seat of the various forms of energy which we meet with in the case of systems obviously consisting of phases which can be separated mechanically, so that considerations applying to coarsely heterogeneous systems apply also to colloidal systems. Although the phases of a colloidal system cannot be so obviously and easily separated as those of an ordinary heterogeneous one, this can be done almost completely by filtration through membranes such as the gelatin in Martin's process. To avoid confusion, however, it has been suggested that the colloidal state should be spoken of as "micro-heterogeneous." There are, in fact, certain phenomena more or less peculiar to the colloidal state and due to the influence of the sharp curvature of the surfaces of the minutely subdivided phase. The effect of this curvature is a considerable pressure in the interior of the phase, owing to the surface tension, and it adds further complexity to the properties manifested by it.

We see, then, that the chemical reactions of chief importance to us as physiologists are those known as "heterogeneous." This class of reactions, until comparatively recent times, has been somewhat neglected by the pure chemist.

In some of its aspects, the problem before us was discussed by one of my predecessors, Prof. Hopkins, as also by Prof. Macallum, but its importance will, I think, warrant my asking your indulgence for a further brief discussion. Permit me first to apologize for what may seem to some of those present to be an unnecessarily elementary treatment of certain points.

It is easy to realize that the molecules which are situated at the interface where two phases are in contact are subject to forces differing from those to which the molecules in the interior of either phase are subject. Consider one phase only, the molecules at its surface are exposed on the one side to the influence of similar molecules; on the other side, they are exposed to the influence of molecules of a nature chemically unlike their own or in a different physical state of aggregation. The result of such asymmetric forces is that the phase boundary is the seat of various forms of energy not present in the interior of the phase. The most obvious of these is the surface energy due to the state of tension existing where a liquid or a gas forms one of the phases. It would lead us too far to discuss the mode of origin of this surface tension, except to call to mind that it is due to the attractive force of the molecules for one another, a force which is left partially unbalanced at the surface, so that the molecules here are pulled inward. The tension is, of course, only the intensity factor of the surface energy, the capacity factor being the area of the surface. We see at once that any influence which alters the area of the surface alters also the magnitude of that form of energy of which we are speaking.

This is not the only way in which the properties of substances are changed at phase boundaries. The compressibility of a solvent, such as water, is altered, so that the solubilities of various substances in it are not the same as in the interior of the liquid phase. It is stated by J. J. Thomson that potassium sulphate is 60 per cent more soluble in the surface film. The ways in which the properties of a solvent are changed are sometimes spoken of as "lyotropic," and they play an important part in the behavior of colloids. We meet also with the presence of electrical charges, of positive or negative sign. These are due, as a rule, to electrolytic dissociation of the surface of one phase, in which the

one ion, owing to its insolubility, remains fixed at the surface, while the opposite ion, although soluble, cannot wander away farther than permitted by electrostatic attraction. Thus, we have a Helmholtz double layer produced.

Before we pass on to consider how these phenomena intervene in physiological processes, there is one fact that should be referred to on account of its significance in connection with the contractile force of muscle. Surface tension is found to decrease as the temperature rises, or, as it is sometimes put, it has a negative temperature coefficient. This is unusual; but, if we remember that the interface between a liquid and its vapor disappears when the temperature rises to the critical point, and with it, of course, all phenomena at the boundary surface, the fact is not surprising that there is a diminution of these phenomena as the critical temperature is approached.

Perhaps that result of surface energy known as "adsorption" is the one in which the conditions present at phase boundaries make themselves most frequently obvious. Since the name has been used somewhat loosely, it is a matter of some consequence to have clear ideas of what is meant when it is made use of. Unless it is used to describe a definite fact, it can only be mischievous to the progress of science.

Permit me, then, first to remind you of that fact of universal experience, known as the "dissipation of energy," which is involved in the second law of energetics. Free energy, that is, energy which can be used for the performance of useful work, is invariably found to diminish, if the conditions are such that this is possible. If we have, therefore, a system in which, by any change of distribution of the constituents, free energy can be decreased, such a change of distribution will take place. This is one form of the well-known "Principle of Carnot and Clausius."

Now, practically any substance dissolved in water lowers the surface tension present at the interface between the liquid and another solid or liquid phase with which it is in contact. Moreover, up to a certain limit, the magnitude of this effect is in proportion to the concentration of the solute. Therefore, as was first pointed out by Willard Gibbs, concentration of a solute at an interface has the effect of reducing free energy and will therefore occur. This is adsorption. As an example, we may take the deposition of a dyestuff on the surface of charcoal, from which it can be removed again, unaltered, by appropriate means, such as extraction with alcohol. Charcoal plus dye may, if any satisfaction is derived from the statement, be called a compound. But, since its chemical composition depends on the concentration of the solution in which it was formed, it is much more accurate to qualify the statement by calling it an "adsorption-compound." Moreover, the suggestion that the union is a chemical one tends to deprive the conception of chemical combination of its characteristic quality, namely, the change of properties. Dyestuff and charcoal are chemically unchanged by adsorption.

The origin of adsorption from surface tension is easily able to explain why it is less as the temperature rises, as we find experimentally. As we have just seen, surface tension diminishes with increase of temperature.

Let us next consider what will happen if the liquid phase contains in solution a substance which lowers surface tension and is also capable of entering into chemical reaction with the material of which the other, solid, phase consists. For example, a solution of caproic acid in contact with particles of aluminium hydroxide. On the surface of the solid the concentration of the acid will be increased by adsorption, and, in consequence, the rate of the reaction with it will be raised, according to the law of mass action. Further, suppose that the liquid phase contains two substances which react slowly with each other, but not with the solid phase. They will be brought into intimate contact with each other on the surface of the solid phase, their concentration raised and the rate of their interaction increased. One of the reagents may clearly be the solvent itself. But in all these cases the rate of the reaction cannot be expressed by a simple application of the law of mass action, since the active masses are not functions of the molecular concentrations, but of the surface of the phase boundaries. The application of these considerations to the problem of the action of enzymes and of heterogeneous catalysis in general will be apparent. That the action of enzymes is exerted by their surfaces is shown, apart from the fact that they are in colloidal solution, by the results of experiments made in liquids

in which the enzymes themselves are insoluble in the usual sense, so that they can be filtered off by ordinary filter paper and the filtrate found to be free from enzyme. Notwithstanding this insolubility, enzymes are still active in these liquids. The statement has been found, up to the present, to apply to lipase, emulsin, and urease, probably to trypsin, and the only difficulty in extending it to all enzymes is that of finding a substrate soluble in some liquid in which the enzyme itself is not. That adsorption is a controlling factor in the velocity of enzyme action has been advocated by myself for some years, but it is not to be understood as implying that the whole action of enzymes is an "adsorption phenomenon," whatever may be the meaning of this statement. The rate at which the chemical reaction proceeds is controlled by the mass of the reagents concentrated on the surface of the enzyme phase at any given moment, but the temperature coefficient will, of course, be that of a chemical reaction.

The thought naturally suggests itself, may not the adsorption of the reacting substances on the surface of the enzyme suffice in itself to bring about the equilibrium at a greater rate, so that the assumption of a secondary chemical combination of a chemical nature between enzyme and substrate may be superfluous? I should hesitate somewhat to propose this hypothesis for serious consideration were it not that it was given by Faraday as the explanation of one of the most familiar cases of heterogeneous catalysis, namely, the union of oxygen and hydrogen gases by means of the surfaces of platinum and other substances. The insight shown by Faraday into the nature of the phenomena with which he was concerned is well known and has often caused astonishment. Now, this case of oxygen and hydrogen gases is clearly one of those called "catalytic" by Berzelius. The fact that the agent responsible for the effect did not itself suffer change was clear to Faraday. I would also, in parenthesis, direct attention to the fact that he correctly recognized the gold solutions which he prepared as suspensions of metallic particles, that is, as what we now call colloidal solutions. Although the systematic investigation of colloids, and the name itself, were due to Graham, some of the credit of the discovery should be given to the man who first saw what was their nature. Adsorption, again, was accurately described by Faraday, but without giving it a name.

I confess that there are, at present, difficulties in the way of accepting concentration by adsorption as a complete explanation of the catalytic activities of enzymes. It is not obvious, for example, why the same enzyme should not be able to hydrolyze both maltose and saccharose, as it is usually expressed. Another difficulty is that it is necessary to assume that the relative concentration of the components of the chemical system must be the same on the surface of the enzyme as it is in the body of the solution; in other words, the adsorption of each must be the same function of its concentration. Unless this were so, the equilibrium position on the enzyme surfaces, and therefore in the body of the solution, would be a different one under the action of an enzyme from that arrived at spontaneously or brought about by a homogeneous catalyst such as acid. This consideration was brought to my notice by Prof. Hopkins, and requires experimental investigation. We know, indeed, that in some cases there is such a difference in the position of the equilibrium position, for which various explanations have been suggested. But it would be a matter of some interest to know whether this difference has any relation to different degrees of adsorption of the components of the system.

At the same time, adsorption is under the control of so many factors, surface tension, electrical charge, and so on, that the possibilities seem innumerable. There are, moreover, two considerations to which I may be allowed to direct your attention. Hardy has pointed out that it is probable that the increased rate of reaction at the interface between phases may be due, not merely to increased concentration as such, but that in the act of concentration itself molecular forces may be brought into play which result in a rise in chemical potential of the reacting substances. In the second place, Barger has shown that the adsorption of iodine by certain organic compounds is clearly related to the chemical composition of the surfaces of these substances, but that this relationship does not result in chemical combination or in abolition of the essential nature of the process as an adsorption. It would appear that those properties of the surface, such as electric charge and so on, which control the degree of adsorption, are depen-

* Opening address by the president of the physiological section of the British Association for the Advancement of Science at the Manchester meeting.

dent on the chemical nature of the surface. This dependence need not cause us any surprise, since the physical properties of a substance, inclusive of surface tension, are so closely related to its chemical composition.

There is one practical conclusion to be derived from the facts already known with regard to enzymes. This is, that any simple application of the law of mass action cannot lead to a correct mathematical expression for the rate of reaction, although attempts of this kind have been made, as by Van Slyke. The rate must be proportional to the amount of substrate absorbed, and this, again, is a function both of the concentration of the substrate and of that of the products. It is, then, a continuously varying quantity. Expressed mathematically, the differential equation for the velocity must be something of this kind:

$$\frac{dc}{dt} = KC^n$$

where n itself is an unknown function of C , the concentration of the substrate or products.

The hypothesis of control by adsorption gives a simple explanation of the exponential ratio between the concentration of the enzyme and its activity, which is found to be different numerically according to the stage of the reaction. At the beginning, it may be nearly unity; in the middle it is more nearly 0.5, as in the so-called "square root law" of Schütz and Borissow, which is, however, merely an approximation. Simple explanations are also given of the fact that increasing the concentration of the substrate above a certain value no longer causes an increased rate of reaction. This is clearly because the active surface is saturated. Again, the effect of antiseptics and other substances which, by their great surface activity, obtain possession of the enzyme surfaces, and thereby exclude to a greater or less degree the adsorption of the substrate, receives a reasonable account. In many cases, the depressant or favoring action of electrolytes, including acid and alkali, is probably due to aggregation or dispersion of the colloidal particles of the enzyme, with decrease or increase of their total surface. It is to be noted that such explanations are independent of any possible formation of an intermediate compound between enzyme and substrate, after adsorption has taken place.

There is a further way in which adsorption plays a part in the chemical processes of cells, including those under the influence of catalysts. It is a familiar fact that the concentration of water plays a large part in the position of equilibrium attained in reversible reactions of hydrolysis and synthesis. A synthetic process is brought about by diminution of the effective concentration of water. There are, doubtless, means of doing this in the elaborate mechanisms of cell life, and, in all probability, it is by adsorption on surfaces, which are able to change their "affinity" for water.

I pass on to consider briefly some other cases in which the phenomena at phase boundaries require attention.

Let us turn our gaze from the interior of the cell to the outer surface, at which it is in contact with the surrounding medium. From the nature of adsorption there can be no doubt that, if the cell or the surrounding liquid contains substances which decrease surface energy of any form, these constituents will be concentrated at the interface. There are many such substances to be found in cells, some of lipid nature, some proteins, and so on. Further, the experiments of Ramsden have shown that a large number of substances are deposited in surface films in a more or less rigid or solidified form. We are thus led to inquire whether these phenomena do not account for the existence of the cell membrane, about which so much discussion has taken place. We find experimentally that there are facts which show that this membrane, under ordinary resting conditions, is impermeable to most crystalloids, including organic salts, acids, and bases. There is no other explanation of the fact that the salts present in cells are not only in different concentration inside from that outside, but that there may be absence of certain salts from one which are present in the other, as, for example, sodium in the plasma of the rabbit not in the corpuscles. Moreover, the experiments of Hoeber have shown that electrolytes are free in the cells, so that they are not prevented from diffusion by being fixed in any way. The mere assumption of a membrane impermeable to colloids only will not account for the facts, since, as I have shown in another place, this would only explain differences of concentration, but not of composition. The surface concentration of cell constituents readily accounts for the changes of permeability occurring in functional activity, since it depends on the nature of the cell protoplasm, and chemical changes of many and various kinds occur in this system. If such be the nature of the cell membrane, it is evident that we are not justified in expecting to find it composed of lipid or of protein alone. It must have a very complex composition, varying with the physiological state of the

cell. Indeed, complex artificial membranes have been prepared having properties very similar to that of the cell.

This view that the membrane is formed by surface condensation of constituents of the cell readily accounts for the changes of permeability occurring in functional activity, since its composition depends on that of the cell protoplasm, and chemical changes of various kinds take place in this system, as it is scarcely necessary to remind you. In fact, the cell membrane is not to be regarded as an independent entity, but as a working partner, as it were, in the business of the life of the cell. In the state of excitation, for example, there is satisfactory evidence that the cell membrane loses its character of semi-permeability to electrolytes, etc. This statement has been shown to apply to muscle, nerve, gland cells, and the excitable tissues of plants, as well as to unicellular organisms. We shall see presently how this fact gives a simple explanation of the electrical changes associated with the state of activity.

If, then, the cell membrane is a part of the cell system as a whole, it is not surprising to find that substances can affect profoundly, although reversibly, the activities of the cell, even when they are unable to pass beyond the outer surface. The state of dynamic equilibrium between the cell membrane and the rest of the cell system is naturally affected by such means, since the changes in the one component involve compensating ones in the other. Interesting examples of such actions are numerous. I may mention the effect of calcium ions on the heart muscle, the effect of sodium hydroxide on oxidation in the eggs of the sea-urchin, and that of acids on the concentration of jelly-fish. Somewhat puzzling are those cases in which drugs, such as pilocarpine and muscarine, act only during their passage through the membrane and lose their effect when their concentration has become equal inside and outside the cell.

The work of Dale on anaphylaxis leads him to the conclusion that the phenomena shown by sensitized plain muscle can most reasonably be explained by colloidal interaction on the surface of the fibers. The result of this is increased permeability and excitation resulting therefrom.

(To be continued.)

Russia's Power Resources

WITHOUT considering the Caucasus, the Trans-Caspian region, or eastern Siberia, there are still in Russia proper great sources of hydraulic energy. In the northwest are the falls and rapids of various rivers—for example, the Volkhov with 30,000 to 50,000 horse-power, the Msta with 30,000, the Narova with 40,000 to 70,000, the eastern Duna 120,000 and the Niemen. In the north, again, the Olonetz region offers a number of available power sites, as do the rivers which flow into the Arctic. In the Ural Mountains energy could be obtained from lakes and from the rivers Chausovaya and Bielaia, and on the Valda: Plateau are sites for power development. In the south and southwest are the falls of the Dnieper, 120,000 to 200,000 horse-power, and the rapids of Dniester and the central Bug.

Most of the sources of power, except in the case of the extreme northern streams, are found in regions thickly settled and already possessing considerable industrial development. Other sources, like the Duna Falls, are on important waterways, and in the case of the falls in the Olonetz region the rivers communicate with centers of power consumption.

Most of these power sites could be easily developed, and current could be supplied over long distances at a low rate. Hydraulic power development would be intimately connected with the improvement of the rivers for navigation and with irrigation.

At present little of this potential power is utilized, except, of course, in Finland. Of the large possibilities, only the Narva Falls are exploited, and these in poor fashion. The capacity of the other twenty or thirty plants rarely runs over a few hundred horse-power, and the bulk of the Russian plants are small affairs of a few horse-power, supplying little factories, saw-mills, etc.; there are also many primitive installations for village mills and similar purposes. A census of existing plants, finished by the Imperial Russian Technical Society in 1913, showed a total developed horse-power in the Empire of 250,000, of which the small plants furnished 80 per cent.

Development is, however, increasing, and better plants are being erected. Thus the importation of turbines climbs steadily, and the annual output of Russian turbines increased from 2,000 horse-power in 1900 to 7,000 in recent years. Large central stations remain extremely rare, but the series of government undertakings, the requests for concessions and the large Stuart project in the Caucasus are encouraging signs. Legislation obstructing the erection of transmission lines needs to be altered, and especially there must be

overcome great national ignorance as to the possibilities in electrical power development, and the lack of knowledge even among technical Russians of the engineering and economic conditions governing hydro-electric installations.

Apart from hydraulic power possibilities, Russia possesses a tremendous resource in the vast peat deposits underlying her many swamps. These deposits constitute 7 per cent of the total surface of the country, and are almost three times as great as the combined peat areas of Germany, Ireland, Sweden, and Finland. From the point of view of agriculture, peat deposits are classed as bad land. They tend to grow and encroach on farm lands, and for this reason, and to protect the public health, they have to be fought continuously.

From the fuel standpoint, however, these peat bogs are favorably situated, being, in general, distant from the oil and coal fields and relatively near the industrial centers. Many plants near bogs have used peat fuel for a long time. As the price of other fuels mounts, more and more peat is used; its extraction has taken on the dimensions of a large industry in many places, and involves the use of machinery. Especially in the Moscow-Vladimir district, where oil and coal are high, a good deal of investigating has been done, looking to the lowering of the cost of peat production and the use of distant deposits. The price of peat near power plants is high, and the government peat lands, when favorably situated, sell for good figures. The difficulty and cost of transportation are a stumbling block in the way of extensive development.

The remedy for conditions is the construction at large deposits of central generating stations with long-distance transmission. The electric energy thus generated could be used also to cheapen the cost of extraction, electrical machinery for the purpose being more convenient and cheaper than steam.

The company which furnishes power to Moscow has undertaken a large project, involving the development of a peat deposit near the city of Bogorodsk. This plant will be built from the experience gained at a German plant in Friesland, near Autrich, where a peat bog is being reclaimed; the peat incidentally excavated is used for power for the excavating machinery and for driving electric ploughs; the bog is to be consumed as fuel little by little; the conclusion will be the transformation of a waste area into tillable land. Another method of utilizing peat when it is rich in nitrogen is to generate gas for internal-combustion engines, and making tar products, from which the fertilized, bi-sulphate of ammonia, is extracted.

The potential importance of the Russian peat deposits for fuel can be expressed in figures. A ton of peat dried in the air to 22 or 25 per cent moisture content has a calorific value equal to half a ton of Donetz coal, or 675 pounds of oil. Extraction, preparation, and air drying costs about \$1.80 per dry ton, but this cost can be lowered by using the electric energy generated. The exploitation of the vast deposits tributary to the center of Russia would lower the cost of fuel by a half, and the same in the northwest. The deposits belonging to the government have been examined, and are found to run about 260,000 cubic feet per acre, equivalent to 2,300 tons air-dried. The area covered by peat deposits in Russia is about 177,000 square miles. If the same ratio holds over the country as for the government lands, the total reserve is about 100,000 million tons of peat. This compares with coal reserves of about 80,000 million tons. The peat is constantly growing, and taking its heating value at half that of coal, it is evident that the peat reserves are about equal to those of coal. Around Petrograd half of the country is covered with peat bogs.

The exploitation of peat as a fuel requires a high degree of special knowledge. The many attempts in this direction in Russia have shown results deplorable from the technical point of view, although satisfactory financially. Continued experience will surely develop the most suitable methods, although adjustment to existing conditions may entail some expense. After the conclusion of the war, great progress in this work may be expected.

The possibility of long distance electric transmission, as it has been developed in modern times, and the success of the scientific utilization of peat, should open the way to the exploitation on an immense scale of the enormous deposits of peat which Russia possesses, and, along with this, the reclamation of worthless districts into agricultural lands.—Notes from an article in the *Revue Générale des Sciences*.

Rail Wear on Street Car Tracks

THE *Electric Railway Journal* states that on a street car line in Chicago which was not used it was found that in 40 months the vehicle traffic wore the rails to the amount of 5 per cent of their life. Other observations give similar results.

Steam Turbines*

An Explanation of Their Principles and Operation

By Charles H. Bromley

To understand the turbine it is essential that one be acquainted with the forms of energy of which it makes use. Energy is of two kinds, potential and kinetic. The former is rest energy, or energy capable of manifesting itself by reason of position, as the weight of a pile driver before it is released to descend, as steam under pressure, confined and ready to move on being released, or as a spring compressed or elongated. Things have potential energy by reason of their position or by the state of arrangement of their molecules. Kinetic energy is energy of motion, as the energy in a falling weight, a moving train, a jet of water or steam. When kinetic energy is mentioned velocity is always implied.

The reciprocating engine uses the potential energy in the steam, for the energy is given up by the steam as it expands, pushing the piston ahead of it. The potential energy is converted directly into mechanical work. A turbine changes the potential energy into kinetic before it does work with the steam. It may make the change complete before the steam enters the moving parts of the turbine, or it may make it in installments—in stages.

DIFFERENCE BETWEEN IMPULSE AND REACTION.

This brings us to the subject of impulse and reaction, that is, to the two ways in which the energy is extracted from the steam at the turbine blades. Impulse action, when related to turbines, means to force, to impel, by impact, as when you wash the floor with water from a hose. The blow, the impact, with which the water strikes the dirt drives it ahead. In an impulse turbine the steam does the same thing to the wheel. Examples of impulse and reaction are shown in Fig. 1. A good illustration of reaction is the common whirling lawn sprinkler shown. The water under pressure flows from the nozzles, causing them to move in a direction opposite that taken by the water. Reaction as applied to a turbine wheel may be explained as a backward push as the steam passing through the nozzle reduces its pressure. The wheels of reaction turbines have blades that form nozzles, and the pressure at the inlet side is greater than that at the outlet. This pressure difference in the wheel is what causes it to revolve. In an impulse turbine the pressure is the same on both sides of the wheel. The two kinds of blading, impulse and reaction, are shown in Fig. 2.

Keeping in mind the two forms of energy, it is well now to understand what is meant by staging as applied to turbines. One of the definitions of stage given in Webster's Dictionary admirably suits our needs:

Stage—"A distance between two places of rest on a road; hence, a degree of advance in a journey."

Steam at high pressure enters the turbine, passes through it and comes out with most of its energy extracted. The steam is on a journey, the turbine is the road and the intervals between stages are the places of rest on the way. If the steam passes through the turbine from the high to the low pressure all at once, if it does not rest, as it were, between the two points, if there is but one distance between the beginning and the end of the journey (expansion), then that turbine is a single-stage machine. If the steam rests more than once on the way, then the turbine through which it passes is a multi-stage machine.

In Fig. 3, left, the pressure due to the total head is applied to the wheel. It is a single-stage machine. At the right the total head is divided into four parts. The machine is a multi-stage one. Each wheel has but one fourth of the total pressure applied to it. The velocity of the water at the nozzles is less in the multi-stage than in the single-stage machine and, therefore, permits of running the wheels slower, although about the same amount of energy is taken out of the jets in both cases. The advantages of dividing the pressure or velocity drop in this way in steam turbines will be taken up presently. A stage in a turbine may also be considered as a compartment for a wheel where the steam decreases either its pressure or velocity, as shown in Fig. 4.

By properly graduating the cross-section of a nozzle you can expand steam from one pressure to another, making the drop between inlet and outlet as much as desired. Such nozzles form the communicating passages between the stationary and moving blades or between the stages or compartments of a turbine. It is in this way that the pressure and velocity are controlled in the wheels and the stages, or wheel compartments.

SINGLE AND MULTI-STAGING.

Primarily, it is the great amount of energy liberated by the expansion of a comparatively small weight of steam that makes staging in turbines necessary. A pound (weight) of steam at 150 pounds pressure expanded

in a perfect nozzle to 1 pound absolute (28 inches vacuum) gives up 325 British thermal units, which is equivalent to $325 \times 778 = 252,850$ feet-pound of energy.

In expanding between these two pressures in one jump the steam would attain a velocity of a little over 4,000 feet per second, or more than 2,700 miles an hour. Nearly all the energy (potential) that was in the steam before its expansion is present after expansion in the kinetic (velocity) form. To convert the kinetic into mechanical energy the steam must be brought to rest by the turbine wheel or rotor.

In an impulse turbine, expansion of the steam occurs only in the nozzles, or stationary blades, and in a single-stage machine, like the De Laval, Fig. 1, for example, the steam is fully expanded in the nozzles and, therefore, it strikes the wheel at the enormous velocity of about 4,000 feet per second.

If the glass in Fig. 1 were moved in the same direction as the jet, or stream of water and at one half the velocity of the stream, the water would just flow over the side of the glass and all the energy in the jet would be extracted. To bring the steam to rest the wheel must run at half the speed of the steam jet, or, for the single-wheel turbine the peripheral speed of the wheel must be 2,000 feet per second. Under these conditions the steam would

leave the wheel with just enough velocity to force itself away from it. To produce this effect, i. e., to get the steam to leave the bucket with no velocity, means using an enormous wheel if a fairly low number of revolutions per minute is desired, or, if a small wheel is used it must run at an extremely high speed. Mechanical difficulties do not permit of obtaining slow wheel speeds, for the wheel would be too large (64 feet diameter for 600 r.p.m.), so small wheels running as high as 30,000 r.p.m. are used in the small-sized single-stage De Laval machines. Gears are used to reduce the speed to accommodate the driven machine. About 500 horse-power is the capacity limit commercially for a single-stage turbine.

Suppose all the velocity were not extracted by the wheel. Then there would still be energy in the steam which might be applied to another wheel and from the second to a third and then to a fourth, all on the same shaft; and so on until the pressure and velocity, and, therefore the energy, were zero. With a suitable number and arrangement of wheels, nozzles and diaphragms (partitions forming the stage compartments) the pressure and velocity changes through the turbine may be controlled as desired. The diagrams, Figs. 5, 6, 7, 8, and 9 show the different methods of extracting the energy from the steam. The page will make a good

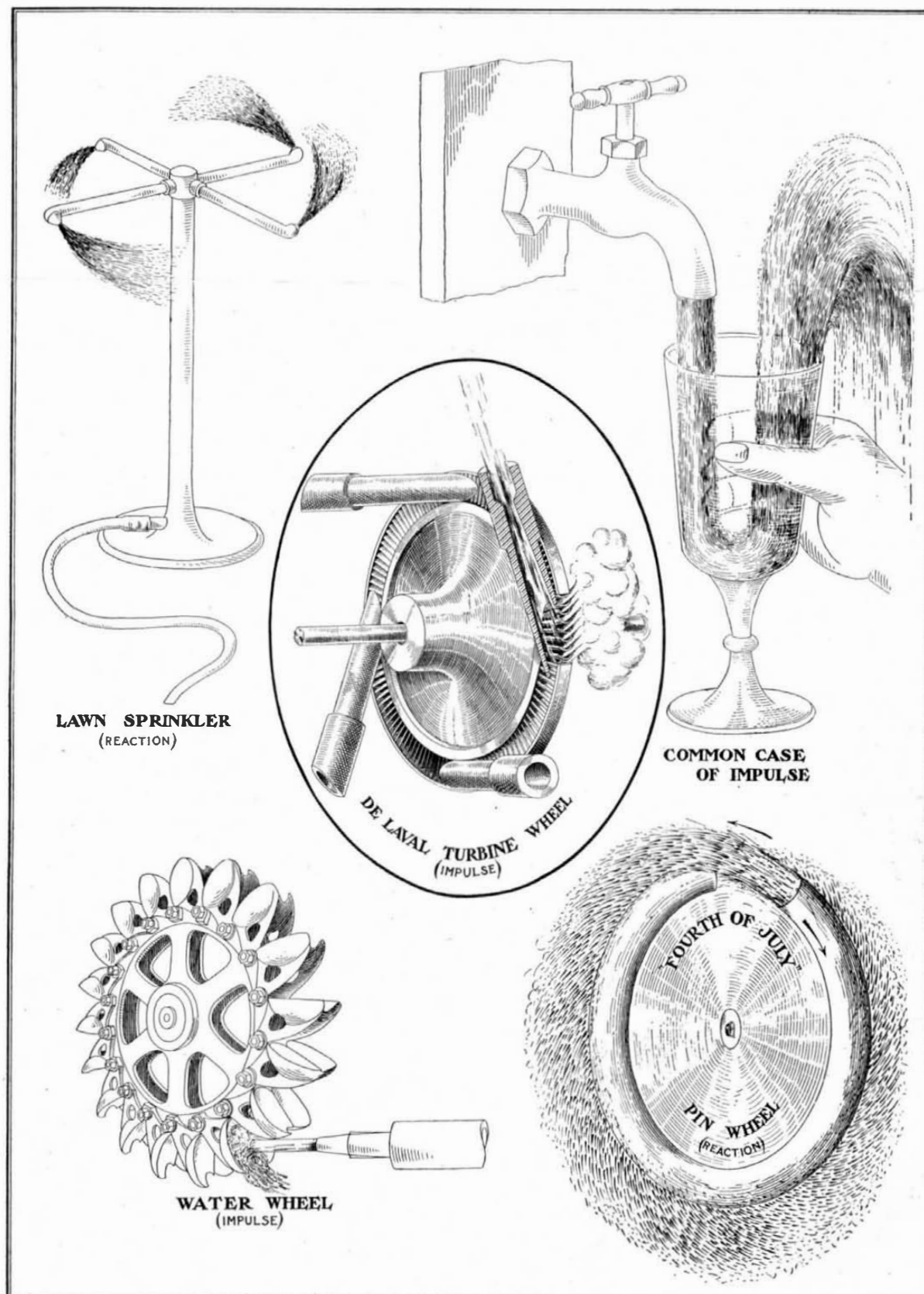


Fig. 1.—Examples illustrating principles of impulse and reaction.

*From a lecture before the Modern Science Club, Brooklyn, N. Y. Cuts by courtesy of Power.

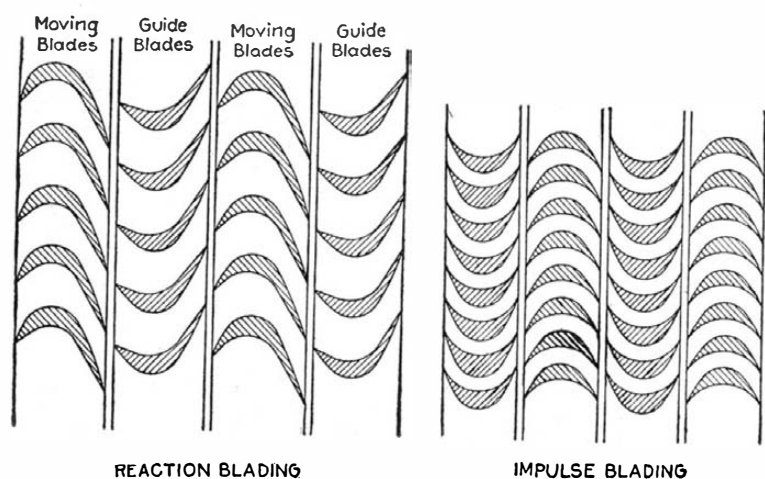


Fig. 2.—Cross section showing turbine blading.

insert for your note-book. The tendency here and abroad is toward the wider adoption of the "composite" design, i. e., velocity staging in the high-pressure end and pressure staging in the low-pressure end. A good illustration of this design is shown in Fig. 9. Note the large drop in pressure in the impulse, or velocity, chamber.

STARTING AND STOPPING.

When steam is turned into an engine it fills the space back of the piston and in some cases the whole cylinder, warming it uniformly and, therefore, minimizing strains due to expansion. In most large turbines, steam would not be admitted around the whole circumference of the rotor when the turbine was standing still unless special "warming pipes" were provided, as they sometimes are. So, to warm a turbine, large or small, it is always best to have all drains open and admit steam quickly enough to revolve the turbine, letting it warm while running. If allowed to stand still with warming steam on, the steam will flow along through the blading in a path, thus creating unequal expansion of, and imposing objectionable strains in, the rotor and casing. If the sealing-gland water is admitted under pressure created by a pump, a tank or from the city mains the turbine may be started condensing. If the gland-seal water pressure is created by an impeller on the shaft whose speed is that of the rotor, and there is no means of sealing, then it is best to start non-condensing, putting the condenser in service slowly after the turbine has attained normal speed. In this way excessive amounts of air are not carried into the machine. Turbines using steam-sealed carbon-ring packing may be started condensing. It is good general practice to shut down the condenser quickly when stopping a turbine, for with some designs of gland seals cold air would be drawn in when the steam was shut off the machine if the condenser were left running, exposing the rotor to distortion, which is objectionable.

TURBINE LUBRICATION.

Lubricating oil for large turbines, vertical or horizontal, is supplied under pressure, the oil being forced by at least two pumps, one driven by the turbine shaft, the other a

ripped off, and if it is a single-flow, Parsons-type machine the dummy pistons and rings will be seriously damaged. The oil circulation system—the reservoir, the pumps, the

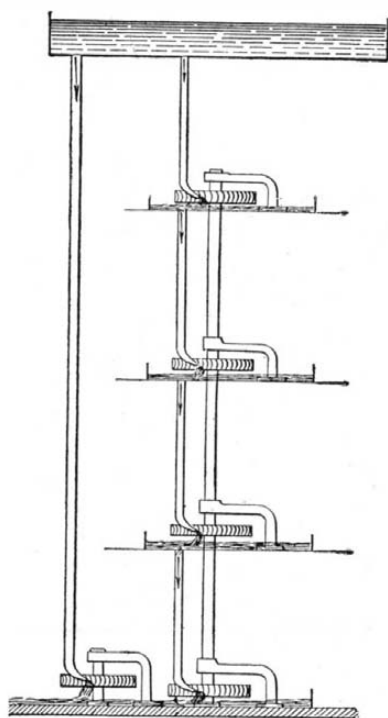


Fig. 3.—At the left is a single-stage wheel, the total pressure being applied on one wheel. At right is a multi-stage motor, only part of the total pressure being applied to each wheel.

filter, the cooler, the pipe lines and the oil grooves—must be given the most thorough attention.

As the oil consumption of turbines is low on account

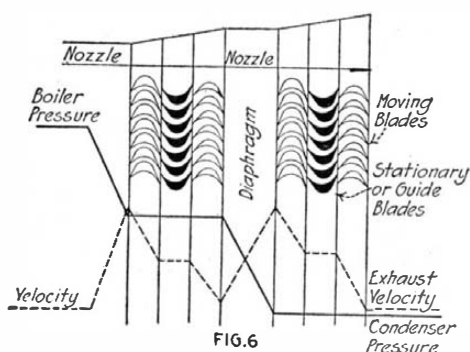


FIG. 6

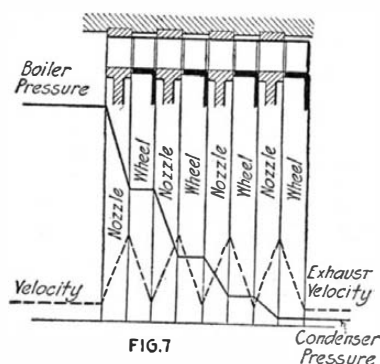


FIG. 7

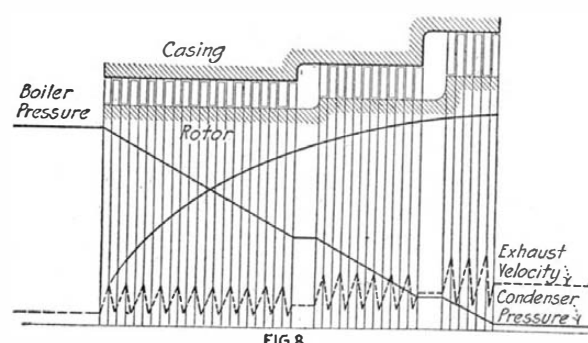


FIG. 8

small, usually duplex, steam-driven pump. The latter should be started before the turbine is turned over to insure good circulation for starting. When the turbine is up to about normal speed the shaft-driven pump goes into useful service and the steam-driven one may be stopped. When shutting down, start the steam-driven pump and let it run until the turbine stops. Sometimes an elevated tank is used for supplying oil for starting and stopping. The aim always should be to have the oil and the oil-cooling water circulating before starting, and continue flowing without cessation until the machine is at a standstill. This is important.

The importance of a continuous oil supply to the bearings of a turbine is much greater than for a reciprocating engine. This is because of the small clearances between the stationary and rotating parts, because the speed is much greater, and because the bearings are near the high-temperature parts of the machine. All of these conditions make a hot bearing much to be feared. Should the babbitt or white metal in the bearings reach the melting point and become plastic, the rotor will drop, owing to its weight, and if not stopped in time many blades may be

of no oil getting in contact with steam or condensate, and because of the circulation system, it is good engineering to use a high-grade mineral oil, free from acids, thickeners, tarry, slimy and saponifiable substances. The General Electric Company recommends that the flash-point, open-cup test, should be below 334 deg. Fahr. and that

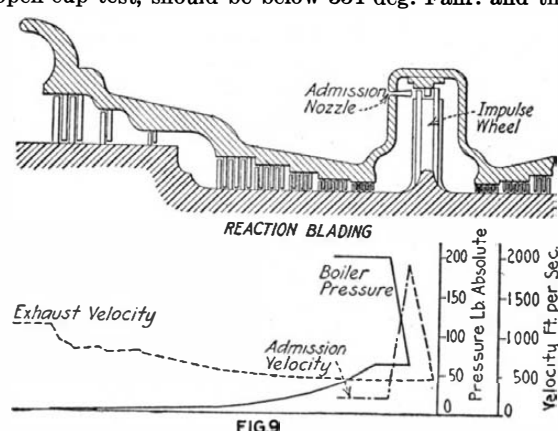


FIG. 9

Fig. 4.—Turbine staging conceived of as compartments. Notice that the openings between compartments increase from the high- to low-pressure end to pass the increasing volume of steam.

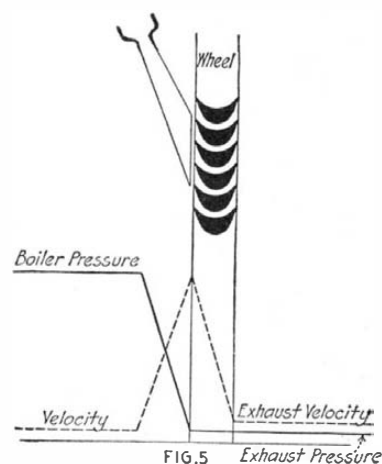
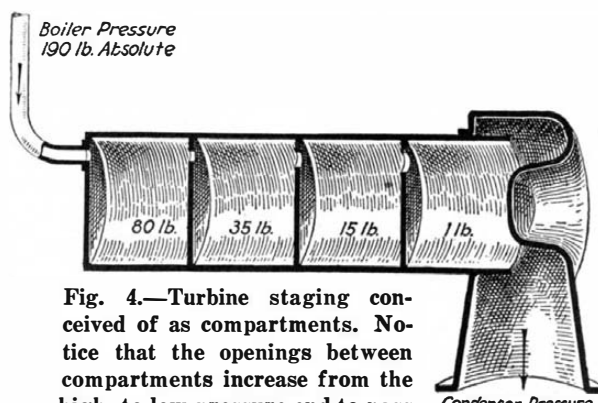


FIG. 5

the viscosity should not be more than 228 seconds at 60 deg. Cent. (104 deg. Fahr.), as shown by a Saybold viscosimeter, which is the kind used by the Standard Oil Company.

Good general instructions for starting are as follows: Have all glands sealed at about 5 to 10 pounds pressure; the atmospheric or free exhaust valve is usually water-sealed. Have it sealed. Have the oil circulating through the bearings. If the turbine is a Curtis vertical, start the step-bearing and valve-gear pumps and maintain the necessary pressure—750 to 1,500 pounds on the bearing, depending on the size of the turbine. Now start the dry-air pump, the hot-well pump and the circulating pump. Usually, there is a pipe leading from the condenser to the top of the circulating pump. Open the valve in this line (priming line), as it allows air to be exhausted from the pump and suction and assists the pump in picking up its water. Slowly bring all pumps up to speed. If there are drains for the different stages of the turbine, open them. Now start the main turbine slowly, increasing the speed and letting the governor get control.

Look around to make sure that the oil and water circulation is good, that the circulating-water pressure and step-bearing oil or water pressure are right, and that the governor has control. Next close the circulating-pump priming valve. Now put on the load. If there are steam-sealed glands, shut off the steam to the high-pressure packing, for the pressure in the first stage prevents air getting in. It may be necessary to regulate the pressure on the low-pressure packing. Now close the drains of the stages. The gear may then be oiled. The main turbine may vibrate considerably while being brought up to speed. Do not be alarmed at this. When this occurs admit a little more steam quickly to get the rotor above the "critical speed," when the vibration will ordinarily cease. Acquire the habit of shutting down the turbine by tripping the emergency governor, which should automatically operate at 10 to 12 per cent above normal speed.

Sometimes, just after the machine gets its load it will lag, i. e., be slow or "jerky" with its speed. Frequently, this is due to the pilot valve for the main steam-admission valve sticking, owing to carbon which has collected on the stem. Pour on some kerosene for the time being, but clean the valves as soon as the unit is stopped. In case of any unusual disturbances inside the casing, as the noise due to rubbing of the blades, trip the emergency governor to avoid serious damage, or, perhaps, a wreck.

For best economy the clearances between the tips of the blades and the casing and between the sides of the stationary and the moving blades, and between the dummy pistons and their rings, if a single-flow, Parsons-type machine, must be small, a comparatively few thousandths of an inch in all cases. Because of the high speeds at which turbines run and because of the small clearances, it is essential that the rotor be in mechanical balance. Adjusting clearances and putting a rotor in balance are jobs requiring skill carefully applied. Time does not permit of taking up these subjects in this lecture, though they are of much interest and importance to the operating engineer.

Nature-Study in Agriculture*

In Relation to Educational Motives and Purposes

By H. N. Goddard, State High School Inspector of Agriculture, Madison, Wis.

WE are told that on the occasion of the visit of a great preacher to Athens, he found the "Athenians spending their time in nothing else but either to tell or to hear some new thing." In education we have had much of this search for new things. The search has led to much foolish waste of educational energy, to many silly fads and to much educational exploitation of children. At the same time it has led to progress. What we need most now and what we have always needed in education in order that real progress may be rapid and sure is *educational balance*—the ability to sift out and retain what is tried and best in the old and unite with it what is sane and reasonable in the new. Changing social, economic and political conditions are bound to call for revised methods and the use of new materials. At the same time, it is necessary to divest ourselves of useless traditions. Our educational system has received and assimilated, with more or less success, many of these new things. Whatever indigestion or educational dyspepsia may have resulted, we have, nevertheless, made rapid growth and, to-day, America may honestly boast of one of the best educational systems in the world, although we may yet have many things to learn from other countries. A long list of hobbies has successively occupied the educational stage. The kindergarten, object teaching, correlation, child study, Herbartianism, recapitulation, industrial arts, Nature-study, plays and games, the Montessori method, vocational education and many more have appeared one after another. We have attempted to apply the psychology of interest and attention, of habit, of sense training and appreciation, of adolescence and of the biogenetic conception. We have striven to make education practical. In these days we are socializing school subjects, motivating our teaching and vitalizing the school. Good has no doubt come from all of these, but the astonishing thing about it all is that the children on whom all of these have been tried, though possibly slightly distorted or intellectually stunted at times, have usually come through in a pretty good state of intellectual preservation. At the same time they have grown up and have been able to meet the duties of life with a greater or less degree of success. All this is perhaps a great tribute to the powers of growth and development in the average child.

Whatever good may have been gained from each of these notions, it is nevertheless true that many leading educators are yet saying that much of our present education is formal, isolated from real life problems, and comparatively ineffective. While I do not wish to assume the part of the critic, yet I think we must confess that there is at least room for further improvement. One of the greatest dangers in all new educational ideas is the tendency to systematize each according to the notion of the adult mind, until most of the life and value have been squeezed out of it for the child. Prof. Charters of Missouri University says in a recent book that every subject when first introduced into the curriculum had a vital value, but that so far, not one has had much life left after submitting to the systematizing process. Nature-study came in response to a keen demand of child-life and child-development, but it immediately fell a prey to the scientists, the "integument men," the anthropologists, the course of study-makers, until its very life was gravely threatened. Fortunately, it has refused to be stereotyped, but as a result, it occupies a comparatively small place in most schools. It has been left for the boy scout movement to really adapt it to the nature of a boy. The fixed programme and the formal class exercise made it impossible for the school to do this.

More recently agriculture has demanded attention and there is much encouragement that this will not only realize its own vital value, but that it may do much in vitalizing all the other school work. There is some prospect that school work in this subject may actually be able to function in the practical life of the community. Nevertheless, there is grave danger that it, too, may be a victim of the standardizing habit, and as a result may lose a large part of its vital value. In order that it may not, it is necessary that we should develop a clear understanding of its values and of the methods and motives which must be depended upon to arouse interest, secure effort and give the work life value. My task is to point out some of these values and motives and show how they become modified as we pass from the Nature-study to the agriculture viewpoint.

Before attempting to do this, let us look for a mo-

ment at the present educational situation. We are trying, in these days, to adjust ourselves to the idea of education in a democracy. This means universal education. As faith in this idea has become deeply fixed, we have been breaking away more and more from old traditions. At the present time, we are asking in educational circles as never before, how can we make education really efficient in meeting the problems of democracy? We no longer look upon the school as an institution for a selected few. The function of the school is, therefore, no longer to train a few people for so-called learned professions, or fit a small number for higher institutions, but it is to provide a training which will best lead every boy and girl into intelligent, useful and successful living. We have come to recognize that our present educational system has tended to train pupils away from the life they are living, rather than to fit them for it. As a result, country boys and girls have too often been anxious to get away from the farm, while young people generally have built up an ambition to find some life easier than their parents have had. A false line of separation has grown up between the work necessary for a livelihood and those activities which contribute to enjoyment. The present viewpoint of education is away from these notions. According to this new viewpoint, the highest product of the schools is not the one who knows the most or who has the greatest mastery of certain subjects. It is rather the person who is most able to meet the duties of life efficiently, and at the same time appreciatively. This means making a living, but it means also the discharging of the duties of citizenship and the capacity for wholesome use of the leisure of life. This viewpoint is well expressed in the ideal of the Danish high schools in the following: "It is not the business of the high schools to give a few facts of this subject or a few facts of that, so much as to awaken the minds of its pupils, to arouse in them a feeling of brotherhood, to give them a knowledge of themselves and of life. We want our pupils to say when they leave: 'Now will I go back to my work more fully realizing the meaning of it and more deeply feeling the dignity of it.'" Such a view seems to demand first of all a general education. This should give command of the tools of knowledge. It should develop right habits and appreciations and put meaning and intelligence into life. It should further prepare for the best citizenship and the highest social service.

In addition to this general education, the school should also provide some training to help every person to be able to gain a competent livelihood in some line, which will not only furnish proper financial support, but which will also be suited to the tastes and talents of the individual. For this purpose the school should help the pupil to find himself with reference to some vocation; that is, he should discover what life activities make the strongest appeal to his tastes and talents. When this is done the school should further provide opportunity for him to develop some skill in the work of this field. This should not be merely mechanical skill, but it should include an intelligent and appreciative understanding of the work. It has come to be the firm conviction of many educators that these two phases of education should not be carried on apart from each other, but they should be so blended that the general education shall furnish a large knowledge and a wide perspective, for an understanding and appreciation of the vocation, while the vocational work helps to vitalize and motivate the general work. These two should not only be closely blended at any particular time or period, but the one should lead gradually into the other as the school course progresses. In the early grades the vocational makes, of course, a minor, and perhaps hardly perceptible, appeal. However, it finds a sudden and rapid awakening in the upper grades, and finally becomes strong and even predominant in the upper years of the high school.

With these views of education before us, I am now ready to consider the main point of my topic. The Nature-study fits, of course, most completely into the early part of the scheme. Its appeal to the child is strong because of its wide freedom and because of its pleasing relations with his own pleasurable activities. The child at this stage is stimulated most strongly through his senses and Nature furnishes an inexhaustible array of new and strange materials which please the eye, attract the ear, stimulate the imagination. Again, all his racial tendencies lead him to love the fields, the woods, the streams and the out-of-doors. Furthermore, since his own organism finds most natural

and most pleasing expression through activity, he finds his most ardent interest in activity in the world about him. Nature, and especially living Nature, furnishes this activity in never-ceasing cycles. This appeal is especially strong because of the constantly changing scenes and situations which Nature affords. A large part of every child's education consists in making conquest of this strange and ever-changing world. The schools have shown far too little recognition of this fact. This interest in activity soon develops an ardent desire to discover what things in Nature can do, and then the child wants to know how they do it. It should be noted that living, changing Nature and the spacious out-of-door make the strong appeal. The school has been exceedingly slow in adapting its stereotyped classroom methods to these well-known child interests. Indeed, much high school botany and perhaps other science, which might have made a strong appeal to interest and effort, has been dead and fruitless because of failure to present this side. It is not information about Nature or even stories that appeal most strongly to the child. What he wants is sympathetic acquaintance with Nature and an understanding of her ways. This should lead to a right attitude which is more moral than intellectual, and which should finally develop both a knowledge and a spirit leading to the preservation of useful things and control of those which are harmful. Educationally this study not only develops sympathetic knowledge, but provides also a most vital intellectual training, and a concrete experience which is able to vitalize much of the more formal work of the school.

As pupils advance toward higher grades, new interests become dominant and should lead to a modification of the work. These new interests take the form of an eager desire to appropriate Nature's resources and to be able to manage and control her forces. Likewise the study of wild animals makes a strong appeal to love of adventure and thrilling experience. Woodcraft finds a ready response. At the same time, the desire for ownership or possession and for the profits of productive enterprise begins to appear and grows stronger as the upper grades are reached. The boy comes to want to be a man and wishes to imitate man's achievements. As this interest becomes predominant, it gives a motive which should gradually modify the work. Gardening work and the raising of plants may well have formed a part of the Nature work considerably before the seventh and eighth grades. Such work as a part of the Nature-study should be given larger attention as the grades advance and should gradually be merged into what may be really called agriculture in the seventh and eighth grades. Formal agriculture should not be started before the beginning of the seventh grade. The work before this time should be generalized with the Nature-study, and not taken up as a distinct subject.

This agriculture of the seventh and eighth grades should not be treated as an informational subject or even as elementary science with simple observation and experiment. There is little motive for such work. It should be treated rather as an industrial art. We hear much about the general culture of a brief informational course in agriculture to help pupils to appreciate farm life and to learn how food products are raised. I am extremely skeptical about this idea. Real motive is lacking and such study will almost certainly lead to indifference if not positive dislike. The only way to appreciate the farm and appreciate how food products are raised is to get into the soil and make it give up, to your labors and care, the golden treasures of fruit, of grain, or of vegetables.

There is already too much appreciation of the farm by those who don't want to live on it but who prefer to wear fine clothes and keep their hands clean in the city. The work should have for its central aim the carrying out of certain surveys and projects relating to farm practice which is adapted to the conditions of the locality. With this practical work, motivated and limited by it, there should be some instruction work. I am not at all certain that any instruction work should be given except as the practical work furnishes the motive and gives the basis for it. Our plan of a daily recitation period carried over the usual school year is poorly adapted to the needs of this work. We have yet to devise effective methods of doing this work in the upper grades. Unless we can do this, agriculture is likely to fail. As a purely informational subject or even as a science subject with suitable experimental work, I have little faith in it, either in the upper grades or in the

* School Science and Mathematics.

high school. Treated in this way it is likely to be made as dead and as devoid of interest as the specialist's type of physics is to the average high school girl. Elementary science, treated with a fair degree of skill, would be far preferable. Even a poor treatment would be better, since this would not drive young people away from the farm. We have had far too much of this kind of agriculture since it has been introduced into the schools. The only motive on which the work can be based successfully is this desire for ownership and possession, and the interest in utilizing Nature's resources for some worth-while result. A boy likes to do any piece of constructive work which brings to him something worth possessing. The interest is heightened in the case of raising farm or garden products by the growth process, which affords interesting change and development from day to day. Again, an exhibit of products and the final sale of what was produced serves to greatly emphasize the worth-whileness of a project, and this strengthens the motive for effort on the part of the pupil. Rivalry in itself is a powerful motive with us all in any activity we engage in. Besides, the boy at this age wants to be a man and therefore to achieve what men are achieving. When he can not only raise more corn or potatoes than his schoolmates, but can beat out his father and the neighbors, the motive again is greatly intensified. All these motives are lacking in textbook or laboratory agriculture.

Again, the agriculture work in the upper grades may be looked upon as of a prevocational nature. The pupil is given a chance to find out what practical agriculture is, and to learn what results may be expected from such work. He thus learns whether this is what he likes or can do most successfully. Later, when he enters high school he is ready for this or for some other line of work.

In the high school it is believed the agriculture should become strictly vocational, that is, it should be for the purpose of enabling the pupil to develop a larger intelligence and greater skill in farm practice, with the definite idea of making this a life work. Not that he must here make any such final decision, but that he may be trained at least for this in case he continues to find himself adapted for it. We have now a number of high schools in Wisconsin where such courses are being given and where, as a result of the course, many boys are planning to make farming their work. Here again the central line of work should be the project in which the student actually carries through some piece of farm practice and, as far as possible, secures a profitable result. Here in the high school, however, the course may be much strengthened and the understanding of problems may be greatly widened by the application of the knowledge of the sciences, of economics and other high school branches. The chief motive, however, will be still much the same, viz., the carrying out of productive work for the securing of a worth-while result. The larger knowledge and better understanding of problems may make some appeal, but this will be secondary. Again, simply studying about agriculture and performing laboratory experiments will fail to make an adequate appeal to the high school pupil.

The laboratory for agriculture should be mainly the soil and the real farm products. Certain laboratory experiments are, indeed, desirable when properly related to actual experience, but agriculture of purely informational and laboratory character has, I believe, no more value and can arouse no greater motive in the high school than an informational course in manual training or domestic science or typewriting. The true place of agriculture, as of these other subjects, is that of an industrial art. Such treatment will not only interest the pupil, but it will have high educational as well as vocational value.

We have tried to show the place of the Nature-study and of the agriculture in the curriculum and have tried also to show how the one merges gradually into the other. We have further tried to show how the Nature-study motive changes, not suddenly, but gradually, until a distinct motive provides the true basis of the agriculture. Nature-study has its large place in the earlier grades, where it should be a generalized study of the child's nature surroundings. The desire to do something for a practical result grows rapidly and leads the pupils to give an eager response to the industrial arts.

At the beginning of the seventh grade, the agriculture makes a most valuable subject for such treatment. The work has a prevocational value in the upper grades, and this gradually changes into more strictly vocational value in the later years of the high school, where the work should still be treated as an industrial art or vocational subject linked up with and strengthened by the general studies of the high school, especially the sciences. There should be definite instruction work, but this should be linked up with and motivated by the practical doing of suitable objects related to the farm. Some of these projects may be school projects, but there

should also be home projects, which actually carry the school work over, so that it functions in the home. It is the business of those charged with agricultural work to devise effective methods of accomplishing these results. The fixed methods of the schools as they are to-day are the least adapted to this work of any of the industrial subjects. At the same time the right kind of agricultural work is a most fundamental need. A purely informational course or a course treated purely as a science is in my judgment of very doubtful value, since it lacks motive. Such cultural value (whatever people may mean by that term) can be obtained far more effectively by the right kind of science work. Agriculture is an industrial art, and treated as such has high educational value, if indeed it is not itself also in the truest sense highly cultural.

The Nitrogen Problem in Arid Soils

STANDING eminent, if not pre-eminent, everywhere, in considerations of soil fertility, the nitrogen problem is especially so under arid soil conditions. The acuteness of the situation in the latter has been recognized, however, by neither the scientist nor the practical man until recently when certain investigations on the one hand, and certain field manifestations on the other, have caused to stand out in sharp relief the nitrogen question from among others in California's soil puzzles. It is with reference to some of these recent findings, and their bearing on problems of soil fertility in California, that this brief paper is written as a forerunner of more detailed discussions soon to appear elsewhere.¹

Considering only the average nitrogen-content of California soils, as based on a thousand or more analyses, the student of the subject does not obtain a true picture of the paucity in nitrogen which characterizes our truly arid soils. For many of our soils are situated in regions of heavy winter rainfall and produce a luxuriant spring growth; hence their nitrogen-content, owing to the large supply of decaying organic matter, may compare very favorably with that of an average soil of the humid region. In our truly arid soils, however, which receive fifteen inches of rainfall per year or less, it is quite the usual thing to find the total nitrogen supply below 0.05 per cent in the air-dry surface soil. Frequently, indeed, under the conditions of the San Joaquin Valley the percentage of total nitrogen in the surface soil may be no more than 0.01 per cent or 0.02 per cent. Therefore, even if all of this nitrogen could be rendered available for assimilation by the plant, the soil could not be expected to produce profitable crops for more than a few years. Fortunately, the roots of plants can draw more or less freely on the nitrogen supply of the soil below the first foot in depth, and thus crops have been produced at times on soils manifestly deficient in nitrogen. It must be remembered, however, that, even in arid soils in which we commonly find nitrification proceeding at the remarkable depth of six feet below the surface, nitrification and hence the available nitrogen supply decreases in intensity rapidly with increasing depth. As a result of a total supply of nitrogen which is too meager, coupled with the relatively small fraction thereof which is rendered available as is pointed out below, nitrogen starvation with its various manifestations in different plants is one of the prominent problems of soil fertility in California, and particularly in case of non-leguminous perennial plants. To illustrate this, it may be mentioned that it has frequently been found impossible to carry young fruit trees through one season of growth in the San Joaquin Valley on soils which are otherwise well supplied with plant food elements, for lack of a proper nitrogen supply.

More frequent even than the total starvation of crop plants on our typically arid soils is the occurrence of plants which languish for several years because of an insufficient supply of available nitrogen. With my co-workers I have obtained experimental and observational data, to appear in detail later as above indicated, which point significantly to a probable causal relationship between the lack of usable nitrates in the root zone and many features of backwardness or disease in our crop plants. These data indicate, almost without exception in the soils studied, that the lack of available nitrogen referred to is to be accounted for in one or more of four ways: First, a lack of sufficient nitrogen in the soil *in toto*; second, a feeble nitrifying power of the soil; third, accumulation of nitrates in the dry surface crust of the soil in which they cannot be used by the feeding roots; and fourth, denitrification of nitrates produced within or added to the soil.

Our investigations point to the conclusion that the second cause, with certain qualifications soon to be indicated, is the most prominent of the four mentioned in connection with the nutritional problems of our crops. We are, therefore, in a position to confirm, as a result of our studies on truly arid soils, Stewart's² statement with

respect to the intensity of nitrification in them, which was based on studies of the more distinctly semi-arid soils of Utah. While we possess ample evidence in support of Stewart's contention in the respect noted, I feel constrained to state that Stewart's criticism of Hilgard's explanation on the humus and humus-nitrogen question as between humid and arid soils is unwarranted by the facts, as we hope to show in detail in our forthcoming publications. The qualification which needs to be made with reference to our assertion as to the feeble nitrifying power of arid soils is that this power is more distinctly relatively rather than absolutely feeble. Thus, we have found that some forms of nitrogen are very readily nitrified by certain arid soils which are not capable of nitrifying other forms of nitrogen at all. For example, the nitrogen of steamed bone-meal or cotton-seed meal or even of sulphate of ammonium is efficiently transformed into nitrate by many of our soils, which will not only produce no nitrate in a month's incubation period out of dried blood or high-grade tankage, but will even cause a loss of nitrate from that already contained in the soil. It appears further that the forms of nitrogen which nitrify most readily in humid soils give the most unsatisfactory results in arid soils as a general rule.

The nutritional factor contributing to the unsatisfactory growth of our crop plants is evidently then, in general, the soil's lack of power to transform enough of its own nitrogen supply or of the supply added in fertilizers or manures into a usable form. We must now give consideration to the theoretical aspects of the reasons underlying the condition just mentioned. There can be but little question that the feeble powers of the nitrifying flora of arid soils is primarily to be attributed to a deficiency in the supply of readily decayed organic matter in such soils. Inasmuch as the organic matter serves as a source of energy for the micro-organisms, its initial small supply in virgin soils of this region coupled with the readiness with which it is depleted by oxidation, must operate to enfeeble and perhaps destroy the nitrifying bacteria. When we remember how small a supply of organic matter we start with in our soils and further that long hot dry seasons are the best of conditions for its dissipation through oxidation, it is small wonder that soil management by methods intended for application under eastern conditions should so far intensify the process, by constant tillage, that the necessary energy supply for the nitrifying bacteria should soon be so low as to render impossible the proper activation of those organisms. To all such direct damage to the soil must be added the indirect damage to the water and air supply necessary for the bacteria which follows the loss of organic matter from soils.

Still other considerations of a theoretical nature enter into the problem. These are concerned with the causes for the unsatisfactory nitrification of the nitrogen in dried-blood, for example. We have noted in all of our experiments that ammonification of dried-blood nitrogen may proceed with vigor in the soils in question while no nitrate is produced. It appears now that in soils which produce ammonia most energetically from dried-blood nitrogen, the nitrifying bacteria are deleteriously affected by the ammonium carbonate and gaseous ammonia which the soils in question appear to liberate in large quantity. Whether this speculation be correct or incorrect will appear from experiments which are now in progress. It appears certain, however, regardless of the outcome of these experiments, that the fermentation of dried blood proceeds very differently in the "normal" and the "abnormal" soils which represent respectively those which nitrify the nitrogen of dried blood and those which do not. In the former soils no odor of ammonia is ever noted in the soil cultures and no other odors but those of active soil are encountered. In the latter soils not only is ammonia given off in large quantities, but it is accompanied by ill-smelling gases resulting from putrefaction.

The brief space of this paper precludes the possibility of a more detailed discussion of the large amount of experimental data which we have accumulated in our experiments with both humid and arid soils; but it may suffice here to point out some of their practical bearings.

1. The addition and maintenance of a good supply of organic matter by green manuring or by the use of barnyard manure must be practised on all soils deficient in nitrogen and organic matter.

2. Nitrogenous fertilizers when employed on such soils must be either of the low-grade organic variety such as steamed bone meal, cottonseed meal, and sewage sludge, or else sulphate of ammonium must be used.

3. The overheating of the soil, excessive evaporation of moisture, and oxidation of organic matter should be prevented through the use of some kind of straw or manure mulch. This is to be regarded as one of the most important measures for present and future soil management in California orchards and vineyards, when nitrogen and organic matter are deficient.—By Charles B. Lipman, of the University of California, in the *Proceedings of the National Academy of Science*.

¹ *Univ. Cal. Pub., Bull. Cal. Agric. Exp. Sta.*

² *The Intensity of Nitrification in Arid Soils, Proc. Amer. Soc. Agron. 4, 132 (1912).*

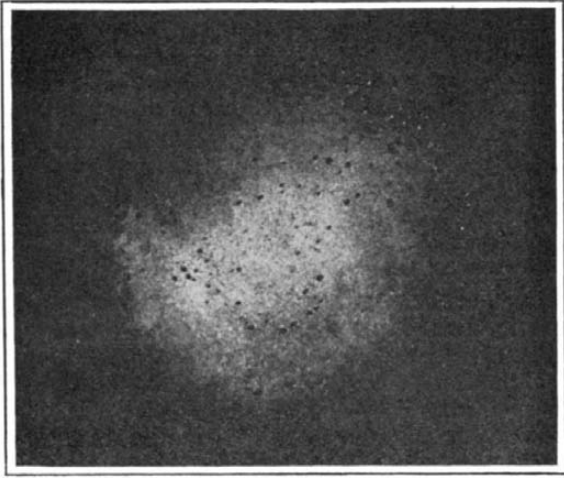


Plate 2.—Film of olive oil at the beginning of its evolution upon pure water (less than one second after the deposition of the drop).

The center is thick (rings and interference colors), the border thin (brown of the first order, 100μ , then paler and paler white). The film is, however, already pierced with circular holes, yet small and rare at the center, large and fused together at the edge.

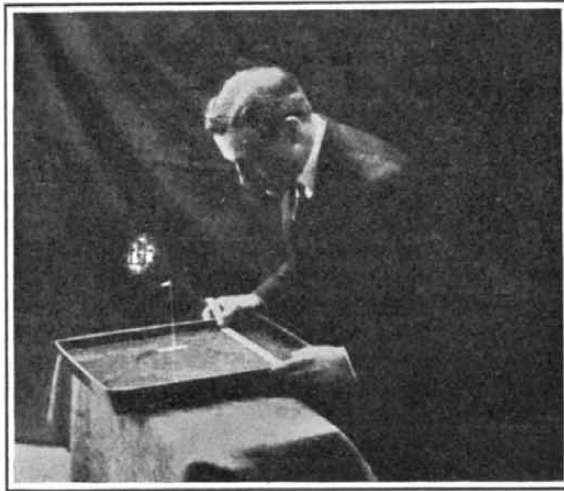


Plate 1.—Boat en route in black tray on water powdered with talc.

A large wake of camphored water free from talc is very visible at the rear of the boat. The operator contracts or expands the free surface by changing the position of the strip of paper placed across the tray.

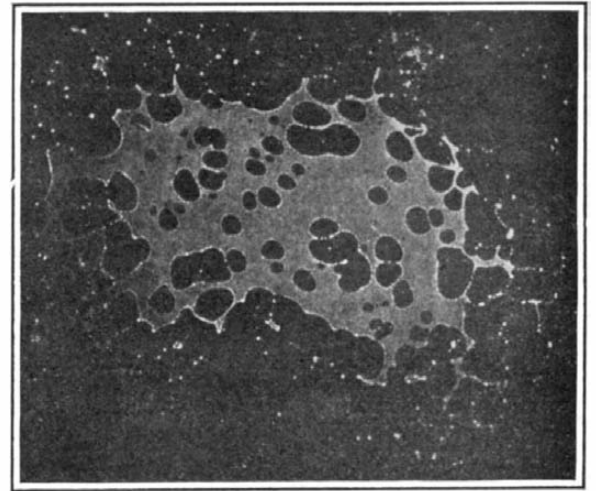


Plate 3.—Film completely extended, age about two seconds.

Its spread has reached the phase when first-order tints appear. A general shrinkage is taking place everywhere. The central black spots have increased in size and fused together; their borders are much broken up and are surrounded by various sized droplets.

Oil Films on Water and on Mercury*

A Study That Tells Us of the Discontinuity of Matter and the Size of Molecules

By Henri Devaux, Professor on the Faculty of Science, at Bordeaux¹

CERTAIN phenomena of daily observation are of great interest to the physicist. Especially so is the expansion of oil over the surface of water or of mercury. I have studied this matter for a long while and from all my observations several unexpected facts stand out.

Films of oil tell us with the greatest nicety of the discontinuity of matter, and the dimensions of molecules. They also give us valuable information as to the field of molecular action. For our observations we will find that there is no need of complicated apparatus; basins, paper, threads of glass, a pipette, a sieve with some talc powder, and finally some oil and benzole suffice for the greater part of the experiments. As to measuring instruments, a double decimeter will do, although its divisions be a million times greater than the diameter of the molecules. Though it seems like measuring microbes with a surveyor's chain, we will see that the measures not only can be made but made with great precision, because of a very remarkable peculiarity of films of the thickness of one molecule. We will yet further see that the smallest variation in homogeneity engenders considerable differences in the surface tensions, causing the molecules to become exactly equidistant.

I. THE LIMIT OF THE EXPANSION OF OIL OVER WATER.

We will first look at an experiment of elementary simplicity yet fundamental. Let us pour some water into a photographic tray and then remove all the impurities from the surface by placing upon it just a sheet of thin paper. Then I scatter on the surface a little talc powder and place upon it a trace of oil by means of a very fine capillary tube. The oil spreads out rapidly from the talc in a circle, since the normal surface tension of the water is considerably lowered. But if there is very little oil, such as the capillary will take up by just touching the stopple of the bottle, the expansion stops suddenly, so that we have a circle of oil surrounded by free water.

Yet is the water really free? Perhaps there are traces of impurities which stop the extension of the oil. This is not the case.

Let us touch with a trace of oil another point distant

from the first one touched; a new circle forms and extends outward from the talc, but the first one is in no way affected. No equilibrating impurity exists outside of the first circle, otherwise its surface would have been deformed and diminished. There is therefore a real limit to the extension of oil upon water. And when that limit is reached the surface tension is both that of pure water and of oiled water.

Let us throw upon this water some grains of camphor dust. At once we see the grains in lively motion, but everywhere with apparently the same speed whether within or without the oiled region.

We may proceed differently. First spread over the water a sheet of oil, powder it, and then try to enlarge a little portion of the oil film by means of a strip of paper placed across it and over the edge of this dish. At once the whole surface is covered, since the layer of oil was somewhat thick. But there always comes a time when the extension stops; the oiled region marked by the talc remains behind, although there is a surface of water free from both talc and oil. The limit is extremely



Fig. 1.—Camphor boat (natural size).

C, grain of camphor at stern;
m, mast amidship.

clean cut and we have side by side two surfaces with the same surface tension—one of free water, the other of oiled water at its maximum extension.²

If at this moment a little camphor dust is scattered on the surface, the grains will be seen in active motion. In getting out of the way of the talc they act like little tadpoles. If the surface is reduced to one half all motion stops suddenly and the talc gathers around each particle of camphor. We may put upon the water a little tin boat such as I devised in 1888,³ and which is shown full size in Fig. 1. A little fragment of camphor is stuck with wax in a notch in its rear. A little mast bearing a streamer is fixed in the middle. This little boat,

²In 1891, Mlle. Pockel pointed out to Lord Rayleigh in a letter published in *Nature* (English) on the 12th of March, p. 437, some experiments relating to these facts. In enlarging progressively a surface of oil upon water or of water soiled with any other impurity, the tension of that surface varies continuously (abnormal condition); it increases slowly at first, then very rapidly, and reaches a maximum. Any further extension from the maximum point leaves the tension invariable (normal condition). If Mlle. Pockel had scattered an inert powder upon that surface to render it visible, she would have realized that, as soon as the maximum is reached, the oil would extend no further.

³See *La Nature*, April, 1888.

placed upon the water, moves rapidly and continuously so as to be seen from all parts of a room (plate 1).

I used this device the nineteenth of April, 1912, in Paris before the Société de Physique. Placed at first upon water with a film of oil at its maximum extension it traveled just as on pure water, leaving in its rear a large wake; the talc was thrown out with a marked vibration whenever it came in contact with the camphor, just as if the camphor corresponded to the propeller of the boat. I diminished the surface. At once the wake became smaller. The boat slowed up. I made the surface yet smaller. The boat stopped. I increased the surface, the boat again moved.

We may thus, by the simple movement of a capillary barrier (strip of paper), show to a whole audience the effect of sudden and considerable changes which the surface tension of water undergoes when covered with a film of oil of the critical thickness. It is a very simple experiment and very effective. Therefore, it is particularly interesting to know what thickness the film of oil must have at this remarkable phase.

II. THE THICKNESS AT MAXIMUM EXTENSION.

(1) *Experimental measures.*—Lord Rayleigh, in his admirable experiments of 1890, tried to find what is the minimum quantity of oil necessary to stop the movement of the camphor⁴ and found an extremely small value, a thickness of about 1.6μ . In 1891 he published the letter of Mlle. Pockel, which we have just mentioned, and in the following year⁵ showed the stopping of the movements of the camphor by a greasy body is due, as the law discovered by Mlle. Pockel led him to see, to a sudden fall in the surface tension of water when the grease layer has the right thickness. In 1899 he published a curve showing the relation between the surface tension and the quantity of oil⁶ and showed that the proportion of oil when the surface tension of the water begins to fall is about one half that at which the camphor movements stopped. The thickness is therefore $1.6/2$ or 0.8μ . But Lord Rayleigh gives it as simply 1μ .

We may obtain a yet greater precision by a method using drops of a standard solution of oil in a volatile solvent. I prepare a standard solution of oil in pure benzole. I use a solution containing exactly 1 cubic centimeter of pure oleine (trioleate of glycerin) per 1,000 cubic centimeter of benzole and a pipette giving 50 drops of this solution per cubic centimeter. Thus a drop contains $1/50000$ of a cubic centimeter of oil, and I place two of these drops upon the water. As soon

⁴Proceedings of the Royal Society, 47, March 27th, 1890. A French translation of the article will be found in *Conférences et allocutions de Sir William Thomson* (Lord Rayleigh), translated by Lugol (1893), p. 48.

⁵Philosophical Magazine, 33, p. 366, 1892.

⁶Philosophical Magazine, 47 and 48, 1899. In obtaining this remarkable curve, Lord Rayleigh appears to have supposed implicitly that the oil on the water always forms a continuous and homogeneous film, even when its surface is much diminished; for example when he gets the quotient of the weight of oil by the surface occupied. This is proper only when the diminishing of the surface is small, say in the ratio of 1 to 1.3. Beyond this limit this process is in error, for the surface begins to assume a globular form, finally becoming a veritable mass of foam. We will speak of this later on.

*Translated by permission from *Revue générale des Sciences pures et appliquées*, Paris, 24th year, No. 4, February 28th, 1913. Reprinted from the Annual Report of the Smithsonian Institution.

¹This article gives a summary of all my researches upon oil films published since 1903; it includes also several new results relating especially to films on mercury and the interpretation of certain observed facts with them. The greater part of the figures have not before been published. The following is a bibliography of my earlier researches: *Recherches sur les lames très minces, liquides ou solides* (Proc.-verb. Soc. Sc. Phys. de Bordeaux, November, 1903); *Membranes de coagulation par simple contact de l'albumine avec l'eau* (I. c., January, 1904); *Comparaison de l'épaisseur critique des lames très minces avec le diamètre théorique de la molécule* (I. c., April, 1904); *De l'épaisseur critique des solides et des liquides réduits en lames très minces* (Bull. des séances de la Soc. franc. de Phys., p. 24, 1904); *Recherches sur les lames d'huile étendues sur l'eau* (J. de Phys., September, 1912, p. 699); *Sur un procédé de fixation des figures d'évolution de l'huile sur l'eau et sur le mercure* (Journ. de Phys., October, 1912). Several physicists have honored me by taking an interest for several years in my researches into molecular physics which has greatly encouraged me in carrying them out. I especially wish to mention M. Ch. Ed. Guillaume, president of the Société de Physique and M. M. Brillouin, professor at the Collège de France.

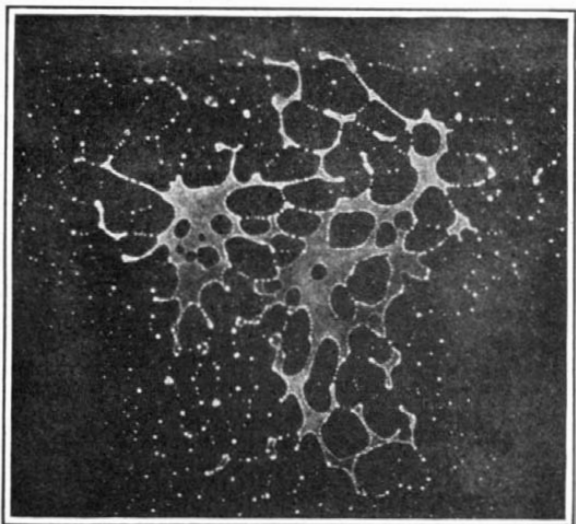


Plate 4.—Very advanced stage in the breaking up and contraction of an oil film by the fusing of the black film and droplets into drops of various sizes.

This film is about three seconds old.

as they touch the water, the drops spread over the whole surface; the evaporation of the benzole is almost instantaneous and leaves a residue of oleine equal to $2/50000$ or 400×10^{-7} cubic centimeter. Earlier measurements showed me that this quantity of oil could not cover all the surface of the tray (625 square centimeters). I blow upon it to gather the invisible film of oil at the farther end of the tray and then scatter upon the nearer end a light veil of powder with the sieve. The talc thus falls upon the free surface of water *E* (Fig. 2); it scatters, carried by my blowing, but you see it stops abruptly along the barrier *TT'*, which though invisible was sharp, and marks the edge of the oil film *H*. The stoppage is of striking sharpness.

I now apply to the portion of water uncovered with oil a band of paper *BB'* (Fig. 3), in order to have a straight capillary border. I now make this barrier approach gently the border of talc which straightens, as is indicated in the figure.⁷ If the barrier is moved a little farther, the talc grains just at the limit of the oil, and more or less distant from each other because they are slightly oily, we see undergo an abrupt closing up between the oil and the paper. Retreat the barrier, and all at once the same grains become free, again floating freely side by side. By means of these sudden changes and by moving the paper slightly back and forth, I can accurately, within a few millimeters, find the limit at which the oil is just slightly contracted, that is at the place where there is the first appearance of change in the tension. At this place I make my measure, determining once for all by my double decimeter rule the length of the film of oil.

(2) *Results*.—We thus get the area of the mean surface covered by the film. In the experiment made the eighteenth of April, 1912, it was 363.71 square centimeters. Now, this was produced by two drops of the oil solution; that is, by 400×10^{-7} cubic centimeters of oil. The thickness of the film was therefore:

$$\frac{V}{S} = \frac{400 \times 10^{-7}}{363.71} = 1.10 \mu\mu$$

with an approximation between 1.04 and 1.15 $\mu\mu$.

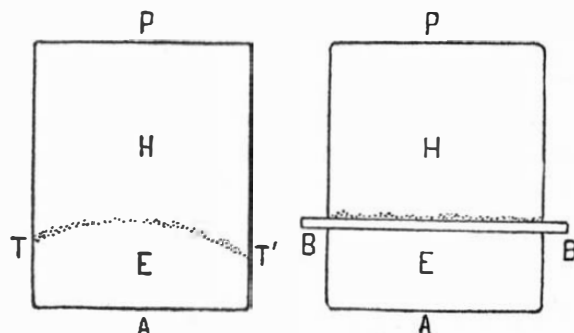
We can then state from this that the thinnest film of oil which can exist upon water is one and one tenth millionths of a millimeter. This thickness, almost identical with that found by Lord Rayleigh, is remarkably small. A simple comparison will give us a better idea of it.

Let us imagine a film of this thickness covering a globe 50 centimeters in diameter; let us enlarge in thought this globe until it has the actual dimensions of our earth. The film enlarged in the same proportion will acquire a thickness of only 26 millimeters, while the paper which covers the globe and upon which the world map was made will increase from its original thickness of 0.1 millimeter to 24 kilometers!

(3) *Comparison with molecular dimensions*.—But we may make better comparisons. In the molecular theory, the thinnest film of any substance which can exist is evidently made of a single layer of molecules; for it is impossible to conceive of a film thinner than a molecule except through the deformation or destruction of the molecule itself.

We possess to-day very numerous and exact determinations of the Avogadro constant, allowing us to calculate molecular dimensions. We have made the calculation for oil, or rather for the trioleate of glycerin. Using Perrin's value for Avogadro's constant, we found 1.13 $\mu\mu$ for the molecular diameter. The theoretical value of the diameter of a molecule thus calculated is practically identical with 1.10 $\mu\mu$, the experimentally

⁷It is yet better to collect the talc scattered upon the free surface by the band of paper itself.



Figs. 2 and 3.—Arrangement for measuring the limiting thickness of a film of oil.

H, film of oil; *E*, free water; *T T'*, barrier of powdered talc; *B B'*, band of paper.

measured thickness of an oil film at its maximum extension. The differences is only in the hundredths of a micron.

We know, therefore, that a film of oil at its maximum extension is formed of only a single layer of molecules.⁸ This remarkable fact is true of other films than those of oil, nor is it limited to liquid films. I have found it to be equally true for various solid substances, with this difference: it is the solid state itself which disappears at the critical thickness and not the surface tension, as with liquids.⁹ I therefore derive this general conclusion: the characteristic mechanical properties corresponding to certain states of a body, the surface tension of a liquid

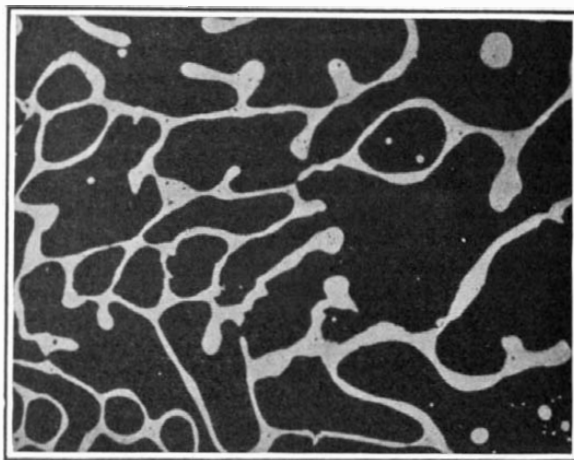


Plate 6.—Great Network of olive oil as generally formed after a long time by a very thick film.

The openings in the network are composed of great black fused films. Here and there are droplets.

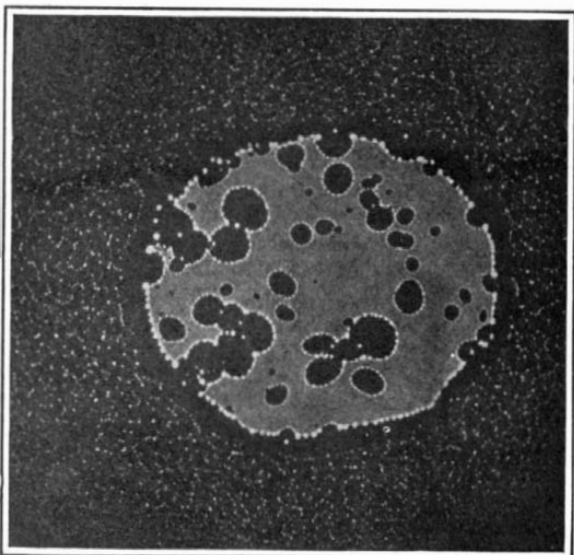


Plate 7.—Film of oleic acid upon mercury. Color, violet-rose (140 $\mu\mu$?).

The surface of the mercury had already received a drop of acid which had entirely contracted into droplets. The new drop expanded very slowly with clearly defined thick borders. These borders have already been transformed into chaplets of great drops such as are always found about the black spots which appear at various moments in the expansion of a film.

or the rigidity of a solid, persist almost intact down to molecular thicknesses, disappearing abruptly the minute we go further.

This fact has a general significance which we should appreciate. For the present, however, we will be content in seeing a new and direct demonstration of the discontinuity of matter and the reality of molecules; it is indeed a new method allowing us to measure the dimensions of molecules with a precision comparable with that of the best methods we have.

⁸Lord Rayleigh in the research cited above discussed this question, but the knowledge then of the value of Avogadro's constant was not so accurate.

⁹Devaux, I. c., 1904.

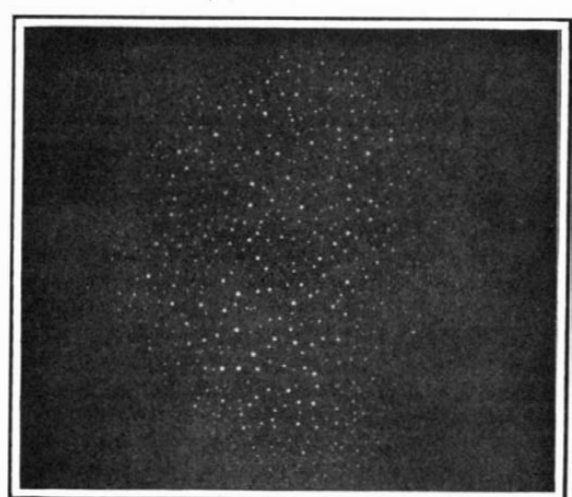


Plate 5.—Final Nearly (') stable state reached after 10 to 15 seconds.

The oil film seems reduced to a cloud of fine droplets scattered over the water. In reality, a very thin, continuous oil film exists between the droplets. The figure of equilibrium of oil on water is therefore discontinuous. (') I say "nearly" because the drops are still undergoing small displacements; they are approaching each other and fusing into larger droplets. This fusion is often hindered by an increasing viscosity, leading to an apparent solidification of the oil in contact with the air.

III. THE EVOLUTION OF LARGE DROPS OF OIL UPON WATER.

Instead of placing upon the water a very minute trace of oil, let us put there an ordinary drop of one to three hundredths of a cubic centimeter. We will now watch a series of phenomena as interesting as what we have just seen. Scarcely does the drop touch the water when it spreads out and covers the whole surface. But the film, of course, is very thick. It is hundreds of molecules thick and clearly visible, because it reflects light better than does water. Generally we see interference colors, at least at one phase of its extension. But this phase is always fugitive, especially with non-drying and fresh oils and when the surface of the water is very clean. This is the case with the present film.¹⁰ The evolution of a film lasts but 10 to 15 seconds; indeed the principal phases take place in the first 3 seconds. However, on water already oily, the formation is very much retarded and the film appears with a sharp circular border, as in plate 7. Soon its brilliant surface is pierced with black circular spots looking like holes, where the water appears as if free from oil. These spots, more or less numerous according to the kind of oil, gradually grow in size, and each one is finally surrounded by a band of small droplets similar to pearls (plate 3).

The first of these spots appears near the edge of the film, where it is thinner than at the center. They grow very rapidly and soon run together. The spots over the rest of the film subsequently behave in the same way (plate 4), so that finally the film is changed into groups of droplets scattered over the surface of the water which reappears as if free from oil, and uniformly dark (plate 5).

It is evident, however, that the surface of the water is yet covered between the globules by a very thin film of oil; and the persistence of this final phase shows that it remains in this discontinuous condition because the oil on the water is almost in static equilibrium. It is therefore necessary to distinguish two phases in the development of an oil film—the evolutionary phase, always fugitive, and the final static phase.

IV. THE STATIC PHASE OF OIL UPON WATER.

Let us consider especially this last phase, that of a very thin, continuous film extended over the surface of the water and studded or not with globules or disks. We will begin by establishing an important fact: the thickness of this continuous film depends upon the existence and dimensions of the globules. Because we find that when a film with minute globules exists beside one with great ones, the first always contracts at the cost of the second. Since, therefore, the tension is stronger in the former, we must conclude that the film with minute globules is the thinner.

With regard to the thickness of thin films, we are then led to distinguish four cases: the maximum and minimum thickness of films without globules; the maximum and minimum thickness of films with globules. Practically these reduce to three cases, since the maximum thickness of a film without globules is necessarily the same as the minimum thickness of one with globules.

(1) MINIMUM THICKNESS OF FILM WITHOUT GLOBULES.

We have already measured this thickness since it occurs in a film at its maximum extension and it is about 1.10 $\mu\mu$.

(2) MAXIMUM THICKNESS OF A FILM WITHOUT OR THE MINIMUM THICKNESS OF ONE WITH GLOBULES.

(a) Principle used in measuring films of a thickness

¹⁰The process of fixation of these films is peculiar and has been described in a special communication (I. c., October, 1912).

greater than that at the minimum: While the minimum thickness of oil films is easy to obtain and even to measure because of the sudden and considerable change in the surface tension for small variations in thickness, this is not the case for thicker films; for when we pass the critical thickness, the surface tension scarcely alters even for very great variations in the thickness of the film. It is therefore much easier to measure a film at its minimum thickness than at a greater thickness.

However, since it is always possible, by enlarging the film, to pass from a thicker to a thinner film, this difficulty can be avoided. We can then in any case choose an oil film without globules having the desired thickness, isolate a portion of the surface, S , then enlarge this to its greatest extension, S' . It will then have its minimum thickness. The ratio S'/S will be the ratio of the two thicknesses. Since the minimum thickness is known, we obtain the other thickness by multiplying by this ratio.

(b) Experimental procedure: In order to determine the greatest thickness of an oil film without globules, I proceed as follows: By means of a glass fiber, I place upon the water of my tray a drop of several tenths of a cubic millimeter. It expands into a film which contracts very quickly into a multitude of little droplets scattered over a black film. I now place a sheet of paper over the greater part of the surface and move it very slowly toward me. Immediately we see the globules over the rest of the surface grow into brilliant disks which finally break up into smaller drops. Repeating this partial wiping away several times, the globules one by one disappear, each momentarily becoming a disk, multicolored or of brilliant white. Finally the whole surface of the water appears black. But there are still very small droplets which may be made evident by slight enlargements made by jerking the dish. Each one gives a flash of light and then disappears. The final phase of the phenomenon requires acute observation, especially for some oils which produce particularly fine globules. In such cases I scatter a light veil of talc powder on the film, then extend the film slightly and at once we see the talc thrown out in little circles about each minute globule.

(c) Results: The following table shows results obtained by the process just described. It gives the ratio between the greatest and least thickness we can have with films without globules.

Trioleine.....	1.32	1.27	1.28
Olive oil.....	1.27	1.21	1.22
Linseed oil.....	1.18	1.15	
Nut oil.....	1.18		
Cod-liver oil.....	1.16		
Sheeps-foot oil.....	1.16		
Castor oil.....	1.53		

The ratio of the maximum to the minimum thickness for an oil film without globules varies a little from oil to oil, but it is always less than two. It is usually very close to unity, so that a film extended over water can have a maximum thickness but little superior to its minimum thickness. We may otherwise state this. A film thicker than one molecule cannot exist without nearly all the excess of oil forming into globules.

(d) The formation of foam in a very shrunken oil film: The last experiment explains a very curious and interesting fact. If we reduce an oil film from its maximum extension so as to diminish its surface to one tenth or one twentieth of its original area the film loses its bright aspect, becoming leaden and as if covered with an exceedingly fine foam. Microscopic examination assures us that the oil has changed into a multitude of droplets of various sizes, 10μ , 5μ , 1μ , and less. Working in the sunlight, I have seen the foam appear before the film has been reduced to one half its maximum extension.

This is a new and direct proof of what we have just learned, that as soon as an oil film is so much reduced in surface that it is more than one molecule thick, nearly all the excess of oil forms into globules.

(e) Variation of molecular distances: This extraordinary fact gives a new and interesting insight into the field of molecular action. It shows particularly that the forces which stretch out these films of liquids are due almost wholly to a single layer of molecules and that the surface layer. It is evident further that a film, if it is uniform, must be greater than one and less than two molecules in thickness. Now, everything indicates that a film is really uniform and homogeneous, since the least variation in its thickness gives rise to considerable differences of tensions which tend to re-establish everywhere a perfect homogeneity, and especially the equality of molecular distances. The difference between the states of least and greatest extension can be dependent then only on the distances between the molecules; if they are compact in the first case, they cannot be so in the second. At any rate, that is the interpretation given by M. Brillouin in a discussion which followed my communication.¹¹ The distance apart of the molecules in such films will be inversely as the square root of the surface. Accordingly, the square roots of the preceding

ratios give the relative molecular distances. This ratio ranges between 1.1 and 1.2.

It follows that as soon as the molecule of a monomolecular oil film are separated by from 1.1 to 1.2 their normal distances, they lose all power of lowering the surface tension of water. Conversely, as soon as the molecules are brought together, so that they are separated by 1.1 to 1.2 of their normal distances, they cause an abrupt and considerable fall in the surface tension of the water, making it practically the same as if it were a large body of oil. For beyond this limit the oil gathers into globules.

(f) Correction to the value of the normal molecular distance: The measure of the molecular distance 1.10μ , given above, corresponds to films at their greatest extension. The true distance in normal oil will be somewhat smaller, say $1.10/1.1$ to $1.10/1.2$ or 1.10 to 0.92μ . This correct distance differs decidedly from the theoretical value, 1.13μ , deduced from the measures of Perrin. Some day we will examine the cause of this difference.

(3) MAXIMUM THICKNESS WITH GLOBULES.

(a) Method of measurement: This measurement is especially difficult. After various attempts, I came to the conclusion that here the only certain method was to proceed by the extension of the films as in the previous case. In order to determine the maximum thickness, I isolate portions of great black spots (4.5 centimeter in diameter) which have appeared very slowly from a thick sheet of oil (plate 6). Then, first lightly powdering the surface, I enlarge it to its maximum extension. This operation is often hindered by the existence of very minute globules. In an instance where the globules were absent I noted that the maximum extension was obtained by about doubling the surface. It certainly was not tripled. We may say, then, that a film of oil at its greatest thickness, when the excess of oil has formed into disks in contact with it, is only about twice its least thickness.

In other words no continuous film will be stable on water when its thickness is greater than two molecules, whatever be the thickness of the masses of oil in contact with it. It will be necessary to await new measures before we truly know whether these films have a real thickness analogous to the maximum thickness without globules. That is, whether they are not formed of a layer of single molecules packed as closely together as possible.

(b) Discontinuity maximum: We are now in the presence of the maximum of the discontinuity of oil films upon water. We may easily have upon the water disks a millimeter or more in thickness. I have noted, for instance, that a cubic centimeter of olive oil placed upon water already heavily oiled forms a disk 30 millimeters in diameter and having an area about 7 square centimeters. Its mean thickness is therefore greater than 1 millimeter, and it is certainly 2 millimeters thick at its central part. Despite this thickness, the disk is surrounded by water on all sides, kept in stable equilibrium by an absolutely invisible film of oil having a thickness one millionth of that of the disk.

A simple comparison will show how peculiar is this discontinuous equilibrium of oil on water: Let us imagine our film enlarged one half a millions times; then our oil film at its maximum thickness would be 1 millimeter thick, and it carries instable equilibrium masses of oil whose thickness can reach and even surpass 1 kilometer (1,000,000 millimeters)!

(c) Comparison with the black film of soap bubbles: I have already, in calling attention to the evolution of a thick film of oil newly formed upon water, spoken of the constant appearance of black circles which grow larger and larger and merge finally into a continuous surface dotted with globules. It is odd that physicists have not been struck long since with the resemblance between these "holes" in the oil films and the black spots of soap bubbles. The mode of sudden appearance, the circular form, size, and progressive enlargement are very similar, and each hole is really occupied by an oil film whose thickness is comparable with that of the black spot of the soap bubble.

The holes in the oil film are, it is true, always more numerous, and further, they finally become surrounded with droplets and then flow together (plates 3 and 4). In reality, soap bubbles often show several simultaneous black spots, especially just before rupture. Further, and which is of special interest, Herbert Stansfield¹² has called attention to black spots in soap bubbles accompanied by collars of disks and granules which correspond to what occurs with oil films, only, since the soap bubbles are never horizontal, gravity necessarily pulls the thick portions away from where they appear. The confluence of the spots is not then peculiar to oil films.

The phenomena in the two cases are the same, the differences arising from the changed conditions under which the films are formed, an independent and two-faced skin in the case of a soap bubble, a skin adherent to and supported by water in the case of the oil film.

Accordingly, the study of the evolution of oil films throws light upon the final stages through which a soap bubble goes when it does not break. It becomes reduced to a black, very thin film, dotted with thick portions, either circular disks or droplets.

Further, similar, very large, black spots have been obtained in the films of soap bubbles by Reynold and Rucker¹³ in their beautiful researches made between 1877 and 1893. Upon these films they determine the thickness of the black spots which were all found sensibly equal and equal to about 12μ . Johannot¹⁴ later showed that films could exist having a thickness one half as great, or 6μ .

We can now compare the thickness of oil and soap bubble films. In both instances we have black films formed from much thicker ones.







Black films of oil with a maximum thickness of 2 to 3μ .

Black films of soap bubbles, maximum thickness of 6 to 12μ .

These thicknesses are of the same order. Oil films are certainly always at least one half as thin as the thinnest soap-bubble films. This important difference must be due to the fact that in the case of oil films on water there is only one free surface.

TABLE OF RESULTS.

The following table gives a summary of the previous results and allows us to make useful comparisons.

THEORETICAL REPRESENTATION OF BLACK FILMS AND OF MOLECULES.		
Greatest and least thicknesses of stable oil films expanded upon water. The thicknesses are multiplied by one million (1 mm. represents 1μ .)		
	1.13 μ	Theoretical size of oil molecules (triosteate of glycerine), ¹⁵ calculated from Perrin's data.
	1.10 μ	Minimum thickness of a stable oil film found experimentally.
	1.15 to 1.53 μ	Maximum thickness of a stable film without globules, or the minimum thickness of a film with globules, found experimentally.
	2 to 3 μ	Maximum thickness of a film in stable equilibrium with great globules or with masses of oil of 1 mm. or greater in thickness.
	6 μ	1st minimum thickness of film of soap-bubbles.
	12 μ	2nd minimum thickness of films of soap-bubbles or maximum thickness of the black spot.

V. OIL FILMS ON MERCURY.

Oil placed on mercury shows very similar results to those obtained upon water.¹⁶ There is still a very sharp limit to the extension, and the thickness of the films at the limits is sensibly the same. When the oil is abundant enough, it forms a thick colored film which grows rapidly with the production of black spots surrounded with globules (plate 7) and finally becomes a very thin film dotted with droplets. Other liquids (sulphuric acid, soap water, distilled water) give upon mercury analogous growths. We have therefore here a very general class of phenomena.¹⁷

VI. CONCLUSIONS.

We see now that a concept which at first seemed chimerical—that is, the reduction of substances to perfectly homogeneous films only one molecule in thickness—has become an experimental reality. And indeed these phenomena work spontaneously and are visible to you all whenever a drop of grease falls upon the water in one of the ordinary plates from which you eat, so that nothing is more common and banal than these extremely thin films.

The formation and stability of these films are automatic. The stability is so great that it is possible, without breaking the film, to distend it—that is, to separate progressively the molecules—until their reciprocal action is entirely destroyed, an operation which we could not perform upon liquids in bulk without leading immediately to rupture.

With our films, however, this is a most simple operation and always successful; it is only necessary to increase the free surface occupied by the film upon the water or the mercury. Thus we have become acquainted with the fundamental fact that the extension of the oil film is limited. As soon as the molecules are separated by a distance greater by one to several tenths of their normal distance they lose all reciprocal action, for they no longer diminish the surface tension¹⁸ of the water. We have

¹²A. W. Reynolds and A. W. Rucker, Proc. Roy. Soc. of London, 1877; Phil. Trans. ditto, pt. 2, 1881, 1883; Phil. Mag., vol. 19, 1885; Phil. Trans. Roy. Soc. of London, II, 1886; Wied. Ann., vol. 44, 1891; Phil. Trans. Roy. Soc. of London, vol. 184, 1895.

¹³Johannot, Phil. Mag., vol. 47, 1899.

¹⁴See Devaux, l. c., November, 1912.

¹⁵Devaux, Journal de Physique, November, 1912.

¹⁶Karl Fischer in his inaugural dissertation (Die geringste Dicke von Flüssigkeitsschichten, Munich, 1896), studied the extension of two oils and other liquids upon mercury. He gives numerous measures of the thickness of films before their rupture. The thinnest had thicknesses less than 3μ (rapeseed oil) and 1μ (sulphuric acid).

¹⁷A curious exception is found in oleic acid and in soap, the molecules of which when stretched over water can be separated some ten times the molecular distance. Devaux, l. c., 1904.

¹¹Meeting of the Société de Physique, May 3d, 1912.

¹⁸Proceedings of the Royal Society, 1906, p. 311.

called this phase the maximum extension. Conversely it suffices to bring them together, by contracting the surface slightly, in order to see the effect of the oil upon the surface tension of the water reappear and increase rapidly, so that the tension passes rapidly from that of pure water to nearly that of oil.

These facts allow us to enter directly the experimental study of the field of molecular action.¹⁹ They allow us to catch a glimpse of other mysteries to be discovered, other marvels to contemplate, and to delve into that domain of invisible elements of which visible matter is composed.

The little drop of oil has much more to show us. Who knows, indeed, but that it will bring us before long phenomena of the greatest importance, yet which at present we can not foresee?

Waste Pine Wood Utilization*

Some of the Products Obtained and Processes Employed

By John E. Teeple

THIS is an old, old industry. As far back as we have definite information, people were using tar on their cordage and pitch on their ships. Even Noah's ark you recall was "pitched within and pitched without," and the ark of bullrushes that supported the baby Moses was "daubed with pitch." We lack positive assurance that a pure pine pitch was used in these cases, but it may easily have been cypress pitch, which is not so widely different. Since the industry is such an old one, the chemist is not to be either censured or credited with its results until within the last thirty years, and more especially within the last ten or fifteen years. The method commonly used formerly was to pile the wood in large heaps, cover it with earth, and by burning a portion of the wood accomplish a destructive distillation of the remainder. The products were tar and charcoal, although some few attempts were made to recover the volatile spirit for use as an illuminant.

About thirty years ago the use of iron retorts was introduced, and this made possible the recovery of an unsatisfactory turpentine, a little of the natural pine oils, and considerable tar oil, creosote oil, pitch and pyroligneous acid, in addition to tar and charcoal. The turpentine had a vicious odor, but being in small amount, it could usually be worked off by persuasion. Tar was a standard commodity, but the trade soon began to differentiate between this retort tar and ordinary kiln tar, and the purchaser demanded a reduction in the case of the former, or refused it. Charcoal could be sold for household fuel, provided the plant was located in the neighborhood of a fair-sized city. Otherwise, it was used to fire the retorts. Gas was also at a time recovered and burned under retorts. When pitch was not readily salable it could be dissolved in the tar oils or creosote oils and sold as tar, but these various light and heavy distillation oils accumulated, and, depending on his ingenuity, the manufacturer worked them up into paint oils, mixed paints, insecticides, disinfectants, fungicides, embalming fluids, medicinal products, and so on until the catalogue becomes alarmingly long. This destructive distillation industry still exists. It is one of the two methods of treating wood to obtain Naval Stores that has been able to operate continuously under even the present very adverse conditions. Many improvements have been made in the type of the retort, in the regulation of heat, and in the separation and preparation of products for the market. In many cases the turpentine now obtained is of excellent odor and of surprisingly good quality, but its success has usually depended on the ability of the manufacturer to work up his oils into lines of specialties under carefully established trade names, and thus protect himself from too vigorous competition. He has improved his retort tar so that now it commonly commands the same price as kiln tar, and is sometimes quoted at a higher figure. With the present high prices ruling for acetate of lime, due to the strong demand for acetone, he is even proceeding in some instances to the manufacture of this product from his pyroligneous acid. A considerable part of these improvements has, of course, been due to chemists, but it must be admitted that a further very considerable part of the preparation of products for the market has been due rather to business men who are good observers, but were not primarily trained as chemists. It seems to me that the destructive distillation of wood is wrong in principle, with our present knowledge of its composition, but at the same time the fact that some of these plants have been continuously operating for many years indicates that they are not to be abolished with the speed that advocates of some of the newer processes have assured us.

Of other processes that have been suggested—distillation with superheated steam, extraction with rosin bath or tar and pitch bath, distillation with water, distillation

with hot gases, digestion with soda and application of vacuum have all had their trial in a commercial way, and a number of them have seemed to operate successfully for a while, due usually to special market conditions, but for the present these have all passed into history. It is very doubtful whether any of them will appear again, at least alone, even under improved conditions. While they lasted, each one found vigorous supporters and provoked much discussion. The question, for example, whether the steam should preferably pass upward or downward through a retort, was considered of considerable moment, but now it hardly arouses our interest. Some chemist usually took an active part in developing all of these processes, but the fact that none of them are operating to-day should not be laid entirely against him. In many cases he was responsible only for the laboratory results, and plants were constructed without the aid of chemical engineers, or, in fact, of chemists or engineers of any kind. In many other cases he had no first-hand knowledge of the industry himself, and relied on faulty information as to cost of wood and market conditions, supplied by men who were promoting the plants. In any case, in developing these processes the chemist and chemical engineer accumulated, and frequently put on record, a fund of very valuable information which is not at all lost, but which will have an important bearing on the future development of the industry.

In one important respect the chemist performed valuable service during this period of development. For the first time there was produced under his supervision a quantity of wood turpentine and pine oil sufficient to have an appreciable effect on the market. He succeeded in making a wood turpentine of a much higher and more uniform grade than had ever been attained before, and by his knowledge of its uses he overcame the prejudice against it, due to its different odor and different source, in enough places so that a firm and steady outlet on good prices was obtained for all that could be supplied. For the first time, too, there was a very considerable amount of the heavy natural oils of the wood, known as pine oil, to be disposed of. This had no regular market, and he succeeded in finding a use for it in a very wide range of industries, where it has so firmly established its value that at the present time the supply cannot begin to equal the demand.

The one other process which has apparently proved of value, and which is still in operation to-day under adverse market conditions in at least two or three plants, is that of extraction by means of a volatile solvent. This method was at one time very extensively employed, producing more naval stores from waste wood than all other systems combined. The amounts of turpentine and pine oil were large and of good quality, and one new product was added from the wood—rosin. This was ultimately refined to a grade approximately corresponding to F and G grades of gum rosin. At first, progress in marketing this was rather difficult, but the oils and tarry matters affecting its use were in part eliminated, and in part the customer was taught what changes were necessary in order to use it as satisfactorily as gum rosins, so that to-day again the demand exceeds the supply.

The worst feature, of course, in the development of this industry during the last few years has been the wide fluctuation in prices. In 1911, F rosin reached a high price of \$8.65 per barrel of 280 pounds, at Savannah: to-day it is \$3—scarcely more than one third of the high figure, and it has been lower. In 1911 turpentine reached a high price of \$1.07 per gallon at Savannah: to-day it is 38 cents and has been lower. Most of these plants were built on the assumption that turpentine would not go below 50 cents per gallon, nor rosin below \$5. These conditions were freely predicted at the time by people who had spent their lives in the naval stores industry, and so probably the chemist should not be blamed too much for the failure of processes to operate successfully at much lower figures, when he had based all his calculations on the higher figures and on the best judgment of people well informed as to conditions.

Now as to the future of the industry: Let us look first at the composition of the material with which we have to deal. Assuming that this is what we know as fat lightwood or as fat lightwood stumps, it contains rosin, turpentine, pine oil and the wood fiber. The problem is: In what way can all these products be extracted and placed on the market to bring the largest net amount to the manufacturer? In some places where the timber has been very largely the long-leaf pine, there is the additional factor of so locating his plant that he can entirely clear the land and largely enhance its value at the same time that he is furnishing his plant with raw material. In the future this will no doubt have an important bearing on the establishment of plants, but it will not be considered here. Suppose we have 5,000 pounds of very rich, fat lightwood stumps. Suppose this contains 20 per cent, or 1,000 pounds, of rosin; 40 gallons, or 300 pounds, of turpentine and pine oil, and 15 per cent, or 750 pounds, of water. This leaves nearly 3,000 pounds of wood fiber. Now, if we subject this 5,000 pounds of fat lightwood to destructive distillation, no matter how carefully, we shall not get all the turpentine and we get

only a small portion of the pine oil, before the rosin and the wood itself begins to decompose. The rosin would be valuable if we could get it, or its decomposition product, rosin oil. The pine oil would be valuable if we could get it, but before either the rosin oil or the pine oil leave the retort in any quantity they become thoroughly mixed with the tar and tar oils from the decomposition of the wood fiber, and there is no convenient way of ever separating them again in marketable conditions from the resulting mess. If we investigate any of the other methods that have been discussed above, we find an important loss in some one or more of the products originally present in the wood. If we digest with soda there is a very fair recovery of the turpentine and a moderately good recovery of the pine oil, but the rosin and resinate are not in good marketable condition, and it would be very difficult to get them in any condition for anything but very special markets. On the other hand, if we use a volatile solvent, properly selected and properly applied, we can recover nearly the whole of the rosin, turpentine and pine oil, and have left the wood fiber unchanged. The rosin, the turpentine and the pine oil will be in such condition that they can be made into the best grades it is possible to produce from wood. The wood fiber is free of rosin, and is in just the condition required for digestion to manufacture wood pulp. According to information and experiments it gives a good yield of a very strong-fibered pulp. Probably it will work up best into what is known as Kraft pulp, or undercooked pulp, and this 3,000 pounds of wood fiber remaining should furnish about 1,500 pounds of good marketable pulp.

Our wood fiber has two disadvantages as a source of pulp. In the first place it cannot be entirely freed from the charcoal and charred and burned wood, and in the second place it will not be entirely free from bark, but there is no question that it will produce a good grade of brown wrapping paper, and with this addition we have made a very complete utilization of our 5,000 pounds of wood. The difficulty heretofore has been that the naval stores manufacturer has approached the problem with the view of making the wood pulp plant an annex to his existing plant. The wood pulp plant is the more expensive, requires the more skilled labor, and is by far the more important, so that the rosin and turpentine production should be considered rather as an annex to the pulp plant, or, better still, the whole should be considered as one complete proposition. Many people have this combination of rosin, turpentine, pine oil and wood pulp in their minds at the present time. There is no doubt that it will be tried before long. It is only to be hoped that when it does receive its trial it will be under the supervision of men thoroughly acquainted with both the wood pulp industry and the wood extraction industry, and with the aid of the most competent chemical engineers there are available. In this way it can build on the mistakes of its predecessors, and it seems to me to stand an excellent prospect of success. There has too much good work gone into this industry, and there is too much accumulated information available, to allow it to languish. I feel sure it has an important future, and when its success ultimately comes, very large credit will be due to the chemist and chemical engineers who have made it possible.

A Test of Clean Milk Production

A WRITER in the *American Journal of Public Health* recounts a comparative test of clean milk production, made under the following conditions: Ten dairymen known by their low bacteria records to be expert clean milk producers were placed on ten dairy farms in the neighborhood of Philadelphia which were ordinarily equipped, and which had only fair records under the owning dairymen. The experts were given sterile cans and sterile covered buckets, with 5 inch openings. Under the conditions of the test they were to milk the cows on the respective farms once, and handle the milk until it was placed either in ordinary tanks of cold water or in ice water for cooling purposes; then, when the milk was transported to the milk stations, bacterial counts were to be made. The result of the test was that whereas the owning dairymen of the ten dairies had bacterial counts on April 5th of 60,000 as a minimum to 4,830,000, the counts on April 6th produced milk which had counts ranging from 800 to 7,000, with a maximum in one instance of 61,000, in which the expert complained that the barn had been swept just before he milked, raising much dust. The author concludes that the fundamentals of clean milk production, which were present in this test, are milking with dry hands into covered milk pails; proper washing and sterilization of milking pails and milk cans; cooling milk by placing cans in tanks of cold water or ice water; and regular laboratory tests of milk for bacteria and payment based on laboratory tests. The last is the essential stimulus to clean milk production. The author says he has revised his opinion in regard to the relative values of equipment and dairyman, so that the dairyman should count for at least 90 per cent, and equipment for the other 10 per cent in clean milk production.

¹⁹M. Brillouin so stated in the appreciation which this professor of the Collège de France gave upon my researches at a meeting of the Société de Physique on the 3d of May, 1912.

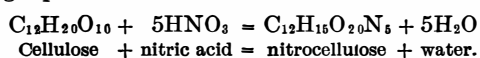
*The Journal of Industrial and Engineering Chemistry.

How Guncotton is Made*

A Brief Description of the Manufacture of An Explosive Much Used in War

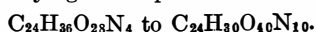
THE nitration of cellulose is the first and the most important operation in the production of guncotton, celluloid and Chardonnet artificial silk. This variety of artificial silk has been superseded, almost completely, by cheaper products made of viscose, or of cellulose dissolved in ammonia-copper solutions, and celluloid has found a formidable competitor in acetyl-cellulose, which is preferred for motion-picture films because it is not inflammable. But guncotton is being made at an unprecedented rate and its manufacture possesses especial interest at this time.

Clean cotton consists almost entirely of cellulose, a carbohydrate whose constitution may be represented by the empirical formula $C_{12}H_{20}O_{10}$ or some multiple thereof. When cellulose is immersed in mixed nitric and sulphuric acids it combines with nitrogen, forming nitrocellulose or pyroxylin (guncotton), according to the following equation:



The only function of the sulphuric acid is to combine with the water formed, and thus to prevent dilution of the nitric acid.

The actual reaction, however, is not quite as simple as this. By varying the composition of the bath and the time of immersion it is possible to form seven distinct compounds, varying in composition from



In practice a mixture of these compounds, which cannot be separated, is always obtained. Nitrocellulose, therefore, is a product of variable composition. This fact explains many difficulties encountered in the manufacture of smokeless powders and the accidents to which some smokeless powders, if improperly kept, are liable.

Nitrocellulose used in the production of celluloid is made of a fine paper resembling cigarette paper, but the guncotton of smokeless powder is always made of raw cotton, usually spinning mill waste, composed of very short fibers which are separated in the carding process. This material is carded again by means of rotating cylinders covered with leather and studded with sharp steel points, which break up all knots or compact masses of fiber. The cotton then goes to the drying chamber where it remains about 45 minutes, carried slowly forward on a number of superposed endless bands and exposed to a current of air heated to 200 deg. Fahr. The dried cotton, containing less than 1 per cent of water,

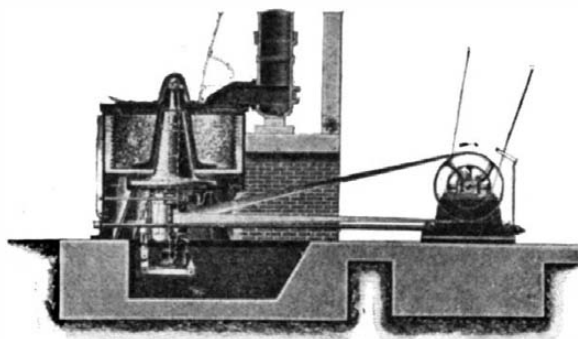


Fig. 2.—Selvig-Lange centrifugal nitrating apparatus.

is packed in airtight iron boxes, in which it is allowed to cool for 8 or 10 hours.

Formerly the cotton was nitrated by simply immersing it in iron or earthenware vessels filled with the acid mixture. The improved methods which are now employed are based either on the English displacement process or on the German centrifugal process.

In the Thomson process, which is employed in the English arsenals, the cotton is nitrated in cylindrical earthen jars, with slightly inclined bottoms, connected in batteries of four jars by lead pipes (Fig. 1).

The cover of the jar is removed and the strong acid bath is admitted through the supply pipe at the bottom. About half a bushel of cotton is thrown in, a handful at a time, and covered with a perforated plate, upon which a little water is allowed to flow from the tank above to prevent the escape of noxious vapors while the cover is being replaced. After $2\frac{1}{2}$ hours the acid bath is drawn off very slowly (about 11 pints per minute), while water is admitted at the same rate. The entire operation occupies 3 hours. Its products are nitrocellulose so well washed that it requires only rinsing with hot water, a spent bath that can be restored by adding fresh acid, and weaker acid solutions that can be made useful by concentration.

The Selvig-Lange process, employed in the principal continental factories, is less delicate and more rapid. About 20 pounds of cotton and 1,000 pounds of acid mixture are put into a centrifugal machine (Fig. 2), so constructed that the liquid flows radially outward through the cotton, downward at the periphery, inward at the bottom and upward in the central part, as is indicated by the arrows in Fig. 3. This circulation is

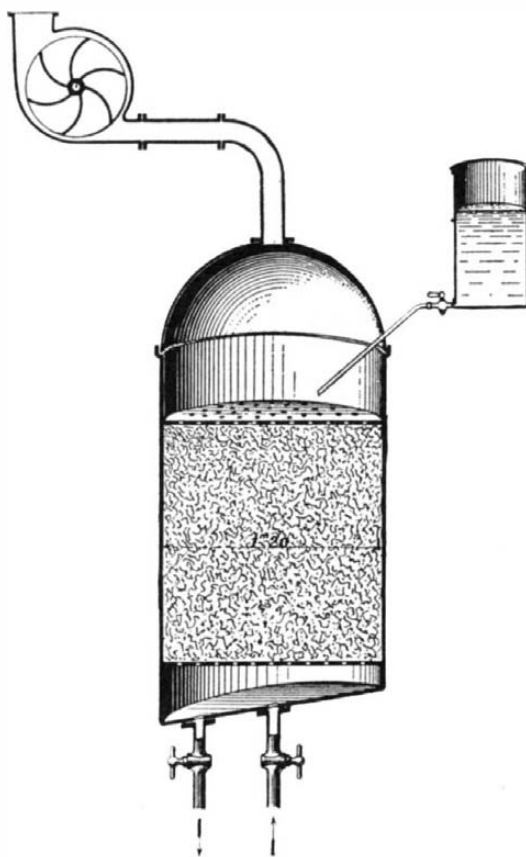


Fig. 1.—Thomson Displacement nitrating apparatus.

maintained for 40 minutes by a slow rotation of the machine (25 revolutions per minute). The outlet is then opened and the liquid is expelled by increasing the speed of rotation. The liquid can be used again after it has been strengthened by adding fresh acid. When the cotton has been nearly freed from adhering acid by 10 minutes' rapid rotation, it is thrown into a conduit and carried away by a current of water.

The nitrated cotton is first washed with cold water and then steeped in boiling water for a long time. This operation, which is essential for the stability of the product, and the mechanism of which is not clearly understood, is conducted empirically, though always with great care, by various methods. In France, the cotton is subjected to 10 steepings, each of 10 hours' duration. In England the same number of steepings are made, but their duration diminishes progressively from 12 hours for the first steeping to 2 hours for the last. Elsewhere the boiling water is made alkaline with lime or ammonium carbonate.

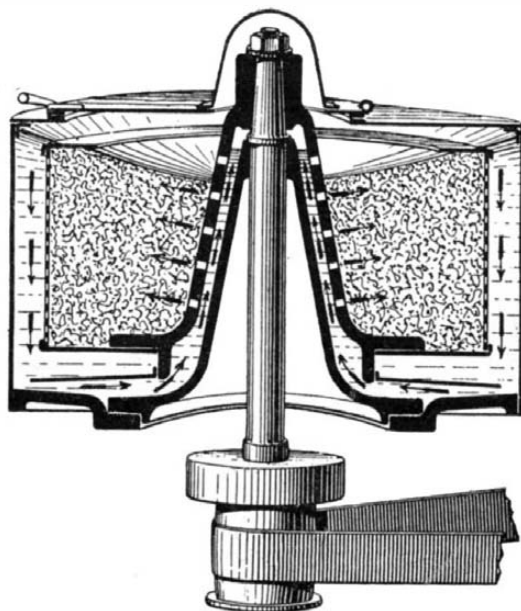


Fig. 3.—Section of centrifugal machine.

The nitrated cotton, which still retains its fibrous form, next goes to a pulp mill similar to those used in making paper from rags. In this apparatus (Fig. 4) the cotton, mixed with a large quantity of water, circulates in a shallow cylindrical tank under the action of a paddle wheel provided with steel blades. The fibers are torn apart and broken up in passing between these blades and a series of fixed blades. The soft pulp thus obtained is diluted with hot water and mixed with pulp derived from preceding nitrations, in order to secure a uniform product. The mixture is caused to flow slowly through a purifying apparatus, where particles of iron are arrested by magnets, and other heavy impurities are retained by the grooved bottom.

Finally the mixture passes through a centrifugal separator which yields a product containing only 30 per cent of water and suitable for the manufacture of explosives, in which, as in the manufacture of celluloid, the nitrocellulose is completely desiccated (by alcohol or hydraulic pressure) only at the instant of use.

Guncotton used in powder factories must contain a suitable proportion of nitrogen, must form solutions of definite degrees of viscosity with mixtures of alcohol and ether, and must pass a test of stability. The heat test, compulsory in France, consists in noting the time required for a prescribed weight of guncotton to give a yellow tint to a specially prepared paper at the temperature of 65 deg. Cent. (149 deg. Fahr.). This time should not be less than 20 minutes. In the preparation of the test paper, 3 parts of corn starch are boiled with 250 parts of water, a solution of 1 part of potassium iodide in 250 parts of water is added, and the whole is allowed to cool. The paper is soaked in this mixture for 10 minutes and dried in the dark. The nitrous vapors emitted by the heated guncotton set free iodine which colors the starch.

The resistance test, also compulsory in France, consists in heating to 108.5 deg. Cent. (227.3 deg. Fahr.) a prescribed weight of guncotton in contact with blue litmus paper until the paper is reddened by the nitrous vapors. This should not occur in less than 7 hours.

In the Bergmann test, which is employed in Germany, 2 grammes of guncotton are heated to 132 deg. Cent. (269.6 deg. Fahr.) for 2 hours in an apparatus which collects the gases evolved. The analysis of these gases should show less than 5 cubic centimeters of nitrogen dioxide.

The production of guncotton is so simple that large quantities can be made in a short time, and the good quality of the product can be assured by rigorous tests. The six national powder factories of France can supply the present enormous demand, and there is no danger of a shortage of chemicals, for France produces annually

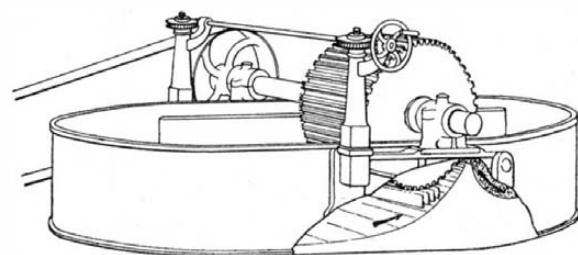


Fig. 4.—Mill for pulping guncotton.

12,000 tons of nitric acid and more than a million tons of sulphuric acid.

Developer for Black and White Copy

A CORRESPONDENT in the *British Journal of Photography* suggests the following formula for ordinary gelatino-bromide plates (the slower the better), to secure great contrasts; and absolutely clear glass in the blacks:

Hydroquinone.....	48 grains.
Sodium sulphite.....	480 grains.
Formaline.....	1 drachm.
Water.....	6 ounces.

It is advised that the copy be lighted very brightly, slightly underexpose the plate, and warm the developer before applying the same.

The slow appearance of the image may deceive the operator into believing it is not going to show at all. But it is like time development, the longer it is left to itself the better the result.

If patience is taken the result will be a perfect black and white negative showing absolutely fogless, clear glass in blacks, and good density in the whites. This developer was proposed by Lumière of Paris, some time ago.

* Translated from A. C. Chaplet's article in *La Nature*.

The Electric Arc in Vapors and Gases at Reduced Pressures*

The Possibilities of a Lamp With Unconsumed Electrodes

By W. A. Darrah

PRESENT commercial arc lamps operate with few exceptions in an atmosphere rich in oxygen or the oxide compounds of the electrodes. As a result the electrodes are oxidized as rapidly as they are vaporized (if not already composed of oxides as in the case of a magnetite arc), and as the oxides cannot be used again commercially it is necessary to provide means for disposing of them. This cycle of vaporization and oxidation of the electrodes naturally results in their comparative rapid consumption, which necessitates the trimming and cleaning of the arc lamp—one of the large factors of arc-lamp operation.

If it were possible to so design the lamp that the supply of material for the arc did not come from the electrodes but from a surrounding gas or vapor, and if in passing through the arc the vapor were not destroyed, it would then seem to be possible to construct an arc lamp which would not require trimming or materially more attention than an incandescent lamp. A lamp of this type, if it had a white light and good efficiency, might in some cases even occupy the field of the present incandescent lamp.

The research, which is described in this paper, was carried on to investigate the possibilities of accomplishing this object, and while the results are very promising from a practical standpoint, they are outlined here for their scientific value and should be considered only as a scientific research.

A study of the light efficiency of an arc from a chemical standpoint shows that there is a certain rather limited class of substances which when introduced into the arc in small quantities produce a very great increase in luminosity. Thus, the addition of small quantities of cerium or calcium compounds to the carbon arc may increase its efficiency over 300 per cent, and the addition of titanium (preferably as an oxide) to the magnetite arc similarly produces an increased luminosity without causing a corresponding increase in energy consumption.

It is a peculiar coincidence that the addition of cerium or calcium to the magnetite arc or titanium to the carbon arc does not result in approximately the same gain in efficiency. The chemical compounds in which the element appears is apparently of little importance.

A study of these facts led to the conception that perhaps an arc could be maintained in a closed vessel and supplied with these light-producing elements in the vapor form. On investigation this did not seem impractical, especially after a consideration of the liquid "inorganic" compounds shown in Table I, which contains some of the elements which produce highly luminous arcs. The table is discussed at length later on in this

paper, but it is interesting to note that titanium, tungsten and other elements which increase the luminous efficiency of an arc, may readily be secured in the form of volatile liquids.

Accordingly, a crude apparatus was arranged in which two hard carbon electrodes were placed vertically above each other in a tight glass vessel, and an arc drawn between the electrodes. As might be expected, this arc was non-luminous and very unstable. Accordingly, a small amount of carbon tetrachloride was poured into the vessel with a rather marked result. The arc then became stable and could be drawn out to several times

A more elaborate apparatus was therefore constructed in which the graphite electrodes were separated by an electro-magnet acting upon an iron core within a glass chamber.

The air was exhausted from the chamber, a small quantity of stannic chloride vapor at a pressure of from 3 to 4 centimeters was allowed to enter and the arc drawn. Under these conditions a stable arc 3 to 4 inches long could be produced with 6 to 7 amperes direct current, and 220 volts impressed. The arc was intensely white and so steady that it had the appearance of a thick incandescent filament slightly bowed and surrounded by a flame-like less luminous shell of yellow. The vapors from this arc, however, soon collected on the walls, forming a dense brown coat, which proved to be mainly tin carbide with a mixture of stannous chloride and other intermediate compounds.

These preliminary tests having indicated possibilities as well as having shown the difficulties to be overcome, additional smaller lamps were constructed along somewhat improved lines.

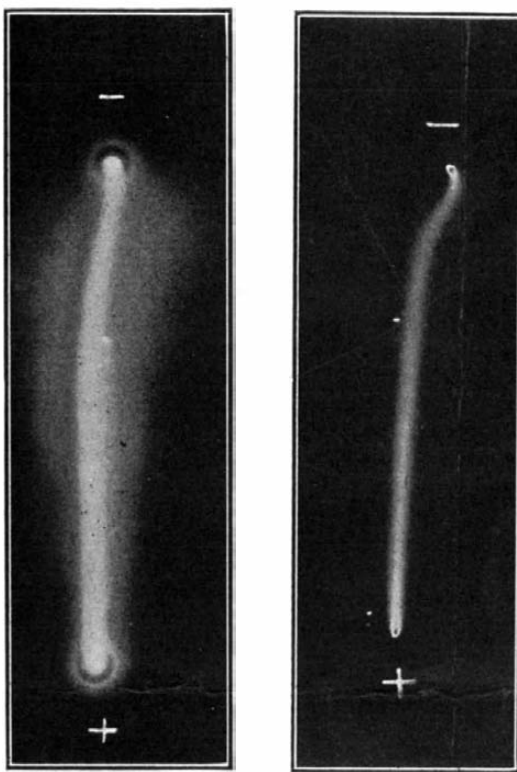
With these a detailed study was made of the effects of the various available electrode materials as well as the different vapors and lamp designs.

For convenience a hard glass (manufacturer's number G-702-P) was employed, as this permitted the sealing of tungsten wires and rods directly into the globe by the use of a flux of potassium nitrate and borax. This allowed the free use of heavy seals which were necessary for the tests. Fig. 1 shows the latest designs which have eliminated many of the difficulties encountered.

The type of lamp shown consists essentially of an arc chamber at the center of which the arc is drawn between two tungsten electrodes about 3/16 inch in diameter. The electrodes are partly surrounded with a refractory insulator, designed to prevent the arc from moving far from the ends of the electrodes, as this allows the magnetic blow of the arc to continue to extend it, ultimately tending to rupture the arc. The refractory insulator also assists in maintaining the electrodes at the very highest temperature, thus increasing the efficiency of the lamp and the stability of the arc.

The upper electrode is fastened by means of a tungsten rod to an iron core, which is surrounded by a glass shell to protect the iron from corrosion, as the vapors used readily attack nearly all metal except tungsten, platinum, gold and a few other inert materials. A flexible tungsten spiral serves to conduct the current from the upper movable electrode to the upper seal.

It was found after a number of trials that a certain combination of gases to be described later gave a minimum amount of "soot" (decomposition products), which gradually collected upon the globe, thus reducing the amount of light radiated. In order to overcome this



Figs. 2 and 3.—Views of new type of arc.

the length which was previously possible, although its luminosity was not much increased. A flaky soot formed by the decomposition of the carbon tetrachloride also filled the glass chamber. A trial was next made with stannic chloride, with a similar increase both in stability and allowable arc length. In this case, also, the luminosity of the arc was much greater. The stannic chloride, however, was decomposed by the air and moisture present, forming a white insoluble powder upon the walls of the chamber, soon shutting out most of the light.

* A paper read before the New York section of the American Electrochemical Society, in joint session with the Illuminating Engineering Society on November 11, 1915. Somewhat abstracted. Cuts by courtesy of Metallurgical and Chemical Engineering

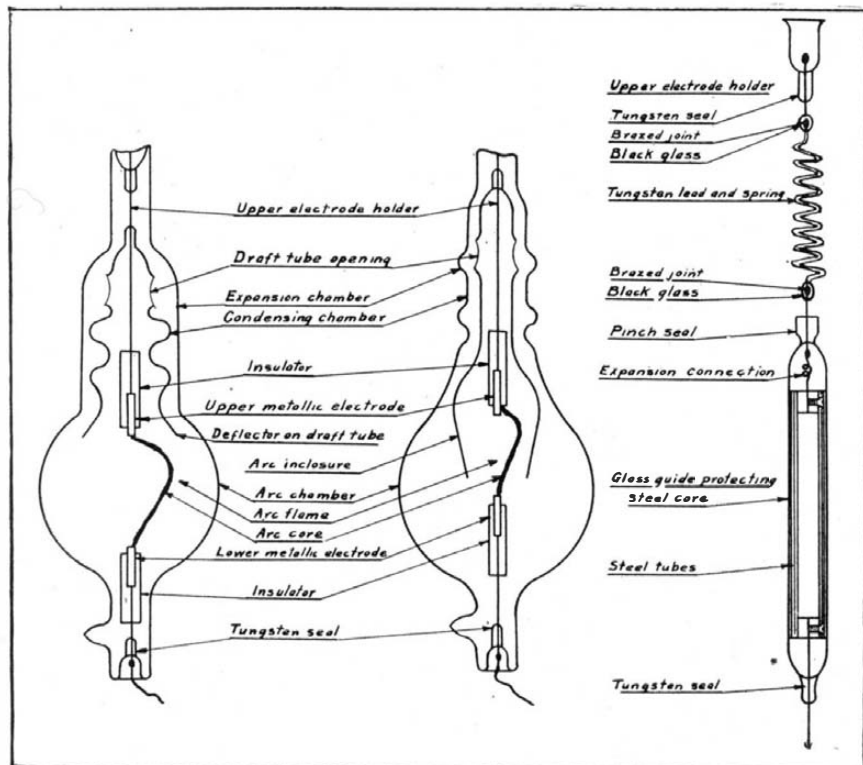


Fig. 1.—Latest construction of new arc lamp type.

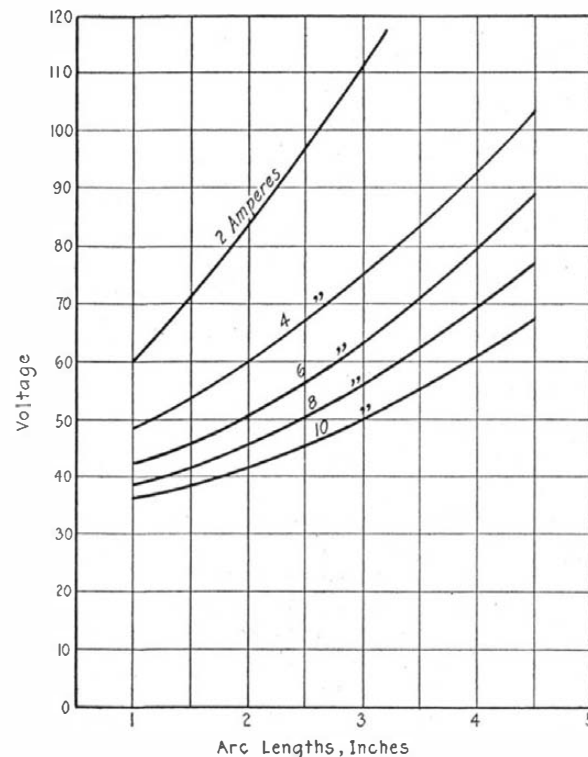


Fig. 4.—Performance curves.

TABLE I.—EFFECT OF VAPORS ON ARC.

Substance.	Boiling Point C°	Melting Point	Effect on Arc	Lumi- nosity	Color
1. Carbon tetra chloride.....	77°	Liquid at ordinary temperature	Stable	Low	White
2. Stannic chloride.....	114°	Do.	Stable	Medium	Yellow white
3. Titanium tetra chloride.....	136°	Do.	Unstable Oscillatory Arc	Very high	White
4. Antimony trichloride.....	220°	Do.	Stable	High	white
5. Arsenic chloride.....	130°	Do.	Stable	Low	Purple
6. Silicon tetra chloride.....	57°	Do.	Unstable	High	White
7. Boron chloride.....	18°	Do.	Unstable	High	White
8. Phosphor trichloride.....	75°	Do.	Stable	Low	Pink and green
9. Aluminium trichloride.....	183°	Volatile	Do.	Low	Yellow
10. Cerium chloride.....	1400°	Do.	Very high	White
11. Calcium chloride.....	1200°	780°	Do.	High	Strong yellow
12. Calcium iodide.....	1100°	740°	Do.	High	Yellow
13. Chromic chloride.....	White heat	Unstable	Low	Green
14. Titanium chloro bromide.....	180°	Very stable	Very high	White
15. Bromine.....	63°	7°	Very stable	Low (high absorpt'n)	Yellow
16. Iodine.....	114°	Volatile	Unstable	Low	Blue
17. Chlorine.....	33°	102°	Stable	High	Yellow

difficulty the arc chamber was extended somewhat above the upper electrode, thus forming a condensing chamber in which the soot could collect, allowing the walls to remain clean.

Further study developed that while this would remove a large quantity of the suspended soot a certain amount was still deposited on the glass walls adjacent to the arc. In order to eliminate this deposit, a draft tube was placed around the upper electrode in such a position that the heated gases from the arc would pass upward through the draft tube out into the condensing chamber and then back downward into the arc chamber for use again. The corrugations shown on the draft tube and condensing chamber have the effect of slightly compressing and expanding the gas as it passes from a chamber of small volume to one of large volume. The alternate expansion and compression of the gases, as well as the contact with the walls thus produced, was found to materially aid the consideration of the suspended matter.

The search for a satisfactory electrode material developed that carbon, either in the form of graphite or in the amorphous state, was unsatisfactory because of the disintegration by the action of the vapors and also the deposit of free carbon which it caused on the walls of the arc chamber apparently by direct radiation, as the draft tube and condensing chamber did not affect it as much as an increase of pressure of the gas around the arc.

It was demonstrated that practically all of the materials available (see Table I) formed carbides under the influence of the arc, and these carbides mixed with free carbon formed so heavy a deposit on the walls of the arc chamber that it was decided to abandon carbon.

Chromium, titanium, molybdenum, nickel, iron, and silver were all tried without satisfactory results. Decomposition of the electrodes, decomposition of the surrounding gases and heavy deposits on the globe made the use of these materials impractical.

The substance which was found to be satisfactory in all respects was tungsten, which proved to be practically inert even at a white heat in the presence of the various vapors used. The tungsten terminals, moreover, did not melt or evaporate in the arc except at a very slow rate, which seemed to be comparable to the evaporation of the filament in an incandescent lamp. A rather interesting phenomena resulting from the gradual evaporation and deposition of the tungsten electrode was exhibited in the growth of a thin star-shaped fringe on the edges of the arc surfaces of the electrodes. This fringe was composed of points 2 or 3 millimeters long, formed of small needle-like crystals of tungsten, and appears to be caused by the slow precipitation of free tungsten from the surrounding gases under the influence of temperature changes.

Having devised a satisfactory construction, it was found that in order to introduce the gases and eliminate air and moisture special methods were required.

As all of the liquids employed are hygroscopic, and many of them readily decomposed by ordinary moist air, it became necessary to exhaust the air from the lamp, heat the lamp and electrodes while at a low pressure in order to remove the air films and then admit the liquids without opening the lamp chamber to the air. This was accomplished by means of a bottle sealed to the lower extremity of the lamp and provided with a ground stop-cock connecting it with the lamp. After the proper degree of exhaustion was reached, the desired liquid was carefully poured into the bottles and the stop-cock opened slightly when atmospheric pressure forced the liquid into the lamp chamber.

The appearance of the arc in this lamp is quite different from other commercial arc lamps (see Figs. 2 and 3).

It is usually very stable, about 1/8-inch in diameter, tubular in form and varies from 2 to 5 inches in length with 110 volts direct current applied, the variations being due to differences in pressure, natures of the gases supplied, etc. A high pressure naturally increases the intrinsic brilliancy of the arc, but makes it necessary to operate at a shorter length as the gas currents due to temperature differences and arc reaction are correspondingly more violent. The diameter of the central luminous tube is also reduced with an increase in pressure.

Some of the arcs revolve very slowly, but as a rule, the low pressure of the gases minimizes the motion of the arc and the general appearance is that of a thick intensely white incandescent filament slightly bent at the upper end. With some of the vapors, as, for example, the metaloid halogen compounds, antimony, phosphorus and arsenic chlorides, the central tubular portion is surrounded by a ragged flame, which is light pink in the case of arsenic and pale green in the case of phosphorus.

The flame portion acts somewhat as an absorbing screen, thus reducing the total useful radiation. It is a curious fact that this flame may exist for a short but appreciable time after the circuit has been interrupted, thus indicating that it probably does not have a part in the conduction of electricity through the vapor, but appears to be a zone in which the vapors after being dissociated by the heat and electrical effects of the arc recombine. The spectrum of the flame is usually quite different from the arc spectrum, and is characteristic of the elements involved, while the spectrum of the arc independent of the ends of the electrodes (which, of course, give a hot body spectrum) is usually a band spectrum, and is practically continuous except for a few absorption lines.

A curious phenomenon noticed with an 8-ampere, 220-volt arc at low pressure in the presence of cerium chloride was a separated arc which gathered into a glowing sphere at one corner of the chamber while the space between the electrodes through which a current of 8 amperes passed was entirely dark.

The complete paper contains typical performance curves which indicate the electrical characteristics of the antimony pentachloride lamp, which is illustrative but does not have as high an efficiency as the titanium tetra chloride or titanium bromo chloride lamp.

Fig. 4 plotted between arc length and voltage, shows the rate at which additional arc lengths require an increased voltage. The curve is also interesting as indicating that a 4-inch arc at 10 amperes requires no more voltage than a 1-inch arc at 2 amperes. In other words, a 10-ampere arc is four times as long and therefore emits four times as much light as a 2-ampere arc. In addition its intrinsic brilliancy is about five times that of a 2-ampere arc. Accordingly, the light emitted by a 10-ampere arc under these conditions is twenty times that of a 2-ampere arc, and since the wattage of a 10-ampere arc is only five times that of the 2-ampere arc, the efficiency is approximately four times that of the 2-ampere arc.

Efficiency curves indicate that 20 amperes are approximately the point of maximum efficiency of this particular antimony pentachloride lamp. It should be understood, however, that the current of maximum efficiency differs widely with differences in the nature and pressure of the gas as well as the volume and available radiating surface of the lamp, and very efficient titanium bromo-chloride lamps have been constructed with a maximum efficiency of about 5 amperes.

Regarding the efficiency secured, it is to be expected that these will vary widely with the condition and nature

of the vapors used, and actual results range from 1 watt permean spherical candle-power to less than one quarter of the value. This performance may be secured with a white light which closely resembles afternoon daylight (north sky). An analysis of the color of the arc with the spectroscope as well as color-matching tests confirm this fact.

As a matter of interest, Table I shows some of the different compounds tested and some of the general results secured. These compounds may be roughly divided into three classes, as follows:

1. The illuminants, or those materials which give a high luminous efficiency. They usually produce unstable arcs if used alone.

2. The stabilizers, or those compounds which have a low luminous efficiency, but when introduced into an arc allow a very stable arc at relatively low voltages.

3. The "catalizers," or those compounds, which are introduced to assist recombination in the flame zone, thus minimizing deposit.

Table I is interesting, as it is the peculiar properties of the compounds, many of which are not very commonly used, that render possible a lamp of the kind described. The problem is to introduce as dense as possible an atmosphere of the various illuminants as titanium tetra chloride into an arc in such a form that it will not be permanently decomposed but may be used again and again. Some of the liquid halogen compounds shown in the table allow this. Some of those compounds (as, for example, those with the metaloids) which have a relatively slight affinity for a halogen are too readily decomposed to be useful. Others, like stannic chloride, are too readily reduced to a less oxidized state, passing from a tetra chloride to the dichloride. Titanium tetra chloride is an example of this condition, but the addition of a small quantity of free bromide to the TiCl₄ (in which it is readily soluble) forms a compound (the bromo chloride) which readily recombines after dissociation.

Fortunately also, since the chloride and bromo-chloride of titanium dissociate at a higher temperature than tungsten chloride, and therefore recombine at a higher temperature than tungsten chloride, these vapors will not attack metallic tungsten even in the presence of the electric arc.

In order to avoid oxidation effects it was necessary to eliminate all oxides from Table I. More complex compounds, such as sulphates, nitrates, could not be considered because of the tendency to dissociate and not recombine. Sulphides, nitrides, phosphides, etc., were eliminated because the chemical stability of these compounds in most cases was too slight to be satisfactory.

Chlorine was the halogen most generally used because of the stronger union of the chloride, and the reduced tendency of the dissociation products to attack the tungsten electrodes.

It would appear that an investigation along the lines here described opens up new possibilities in light production, but it cannot be too strongly emphasized that while the results set forth in this paper offer considerable promise from an applied, practical standpoint, yet they are not presented for consideration as representing a finished device, but merely a research in what seems to be a new and interesting field.

Repelling Attacks of Aircrafts

EVEN before the great war began it had been recognized that aircraft of various descriptions would be made use of in warfare, and that some means of defense would be necessary; but no definite plans had been formulated except by the Germans, who had designed some rapid-fire guns, so mounted that they could be trained at any angle up to a vertical fire. Even in the German equipment, however, there was evidently not a very great number of such weapons, as is evidenced by the illustration on the first page of this issue, which shows how some German soldiers improvised an anti-airship gun by so mounting a rapid-fire field-gun that it could be fired at a very high angle, and it will be noted that the entire gun, with its regular carriage, has been elevated upon a rudely built conical foundation in such a way that the gun can be swung around to point at any part of the sky except a small portion directly overhead.

As a matter of fact, the defense against aircraft by guns fired from the earth has not proved very effective, although a number have been destroyed by this means, and the most satisfactory way of repelling raiding airships and aeroplanes is by big, high-powered aeroplanes capable of carrying a good-sized gun, as well as a gunner, in addition to the regular pilot.

When firing from the ground, even a Zeppelin offers a very small mark when at an elevation of several thousand feet, and, in addition to this, the rapid movement of the ship makes the task of making a hit vastly more difficult, and these difficulties are greatly increased in the case of an aeroplane.

Electric Activity in Ore Deposits—II*

Complicated Conditions and Some of the Results

By Roger C. Wells

Concluded from SCIENTIFIC AMERICAN SUPPLEMENT No. 2087, Page 16, January 1, 1916

DETAILED STUDY OF VARIOUS POTENTIALS.

The object so far has been to establish and exemplify the proposition that electric currents may be generated in the earth and bring about chemical effects. We must now, somewhat more theoretically, consider the relations between electromotive forces and minerals, and must attempt to explain them consistently and point out the conditions under which they are constant and reproducible. In this connection, it may be mentioned that measurements of electromotive force are quantitative expressions of physical or chemical differences between different systems—differences made evident by a proper separation of the systems. When the systems are properly separated the tendency toward electric equalization between them may easily be measured. By union or mixture of the systems the differences would generally be equalized without visible electric action.

The most general statement that can be made about the potentials shown by minerals in different solutions is that the potentials are chiefly determined by the solutions. Without denying that there may be specific effects due to the minerals themselves it may be positively stated that the effect produced on the potentials by changing the solutions is enormously greater than the effect of changing the minerals. This is, of course, due partly to the fact that wide variations in the concentrations of the effective constituents are possible in different solutions.

The very great similarity of all the potentials noted with mineral electrodes to "oxidation and reduction" potentials has already been pointed out. When substances capable of giving such potentials to inert electrodes are present in relatively large amount in a solution in contact with minerals, very constant potentials may generally be developed, but the action of the mineral is then scarcely more than that of an electric conductor, as the amount of oxidizable or reducible material in the solution is so large. Such combinations are not adapted to show differences between minerals, although the data obtained by the experiments may aid in elucidating the chemistry of ores.

Of course, all minerals have some solubility, so that no matter what other substances there may be in a solution the products resulting from the minerals must also be present. As these products are in general oxidizable or reducible ions, the conclusion is inevitable that the potential of most minerals will be of the nature of an oxidation and reduction potential. We thus return to the thought that even if the minerals have specific potential differences the effect of their solution products on the potential can not be neglected, and this effect may, in fact, be all there is to the "potential of a mineral" in water. If pure water could be saturated with only the solution products of a pure mineral the problem would be easy, but in practice the complete removal of foreign substances from the water and the mineral is extremely difficult if not impossible.

The potential shown by some specimens of a given mineral depends considerably on the previous treatment of the specimens, the explanation of the differences found being that if a mineral is long immersed in a solution some of the solution penetrates its invisible pores and subsequently diffuses out very slowly when the mineral is placed in another solution. When once the pores are filled with water or an indifferent electrolyte the mineral is almost as responsive as a platinum electrode to changes in acidity or concentration of the solution; that is, to such changes as determine the equilibria of the effective ions in the solution.

CORRELATION OF THE MEASUREMENTS OF POTENTIAL.

The study of the potential of various combinations of solutions and minerals has so far merely opened up a large number of new problems, whose complete elucidation will require further study. Enough has been done, however, to establish the position of several minerals in the electromotive scale. It has been shown that oxidizing, reducing, acid, and alkaline solutions in contact with minerals impart widely varying potentials to the minerals. Neutral salts, however, have less effect and it seems reasonable to conclude that the potentials shown in neutral salt solutions which are not markedly oxidizing or reducing are practically identical with the potentials that the minerals would assume in pure water—that is, they are due to the solution products of the minerals. The chief sources of error in obtaining such potentials are: The presence of impurities in the mintue

fractures and pores of the minerals; the fact that the atmospheric environment is not, in general, in equilibrium with the minerals and their solution products; and the extreme slowness with which the very insoluble minerals attain equilibrium with solutions in contact with them.

It is obvious that the ions formed by the solution of most minerals in water fall into the class of easily oxidizable or reducible substances. The mineral potentials are therefore "oxidation and reduction potentials."

Ore deposits are likely to be the seat of countless differences in electric potential between both ores and solutions, the whole system being unstable and subject to continuous change. Geologic changes expose large areas to chemical attack. Chemical differences thus produced will generate electromotive forces, which, if opportunity is afforded, will produce currents operating to equalize the differences in potential. Diffusion in and through the solutions will also generate feeble electric currents and, conversely, electric currents may influence the diffusion and transference of matter. The greater electric conductivity of solutions as compared with conducting minerals will probably restrict the currents to solutions wherever two courses may be possible.

If a particle of ore without electric potential could be transferred in that condition to a solution it would at once assume an electric charge. Without attempting to explain this phenomenon, one may say that the particle of ore has become slightly polarized and will remain polarized until the system is reduced to electric uniformity by chemical action or until there is an addition or subtraction of electricity. While it is in the solution the ore will be protected somewhat from chemical attack or, on the other hand, it may be made more liable to attack, according as the polarization is positive or negative. If a current is generated a chemical change will occur either in the ore or in the solutions bathing the ore.

It has been shown that when the current is in the direction "solution to ore" the chemical change is a "reduction." Conversely, a current from ore to solution must be accompanied by oxidation. Whatever may be the course of the current, secondary reactions may cause the precipitation of insoluble films on the minerals that form the electrodes.

It is conceivable that differences in degree of polarization might affect the growth or solution of minerals and thus lead to variation in crystal form, distortion, unequal development of the different faces, and like effects. The polarization need not be caused wholly by the solution immediately in contact with an ore; it might be the result of electric activity at another point, the current being transmitted through the conducting ore. Though crystallization and solution are affected by foreign salts in solution no attempt has been made, so far as I am aware, to correlate these effects with electric conditions, partly, no doubt, for the reason that the crystallization of electrically conducting minerals can not be studied under conditions as favorable as those available for the study of the crystallization of more soluble substances. If it is granted that different crystal faces have different solubilities this fact would demand as a corollary that there should be different degrees of electric polarization on the different faces.

Electric activity is most likely to come into play in ore deposits, however, when a single mineral or body of ore is bathed by different solutions at different places. The electric circuit afforded by such conditions would be like the following cell:

+Pyrite / acid ferric sulphate / potassium chloride / sodium sulphide / pyrite —

If, on the other hand, two different minerals are involved, the cell may be of a simpler type, like the following:

+Marcasite / potassium chloride / galena —

or

+Marcasite / potassium chloride / sodium sulphide / pyrite —

At each of the above electrodes some local action, either chemical or electric, would doubtless occur immediately; there would remain a residual potential, however, which would be available for producing further effects, possibly at more or less remote points.

If a considerable mass of ore is in contact near the surface with an oxidizing solution—for example, acidified ferric sulphate—and at depth with a less oxidized solution—as ferrous sulphate (there being also any circuitous liquid connection)—electric action should result in the oxidation of the lower solution and reduction of

the upper solution until equilibrium is attained. The current would pass downward in the solid conductor and upward in the electrolytic conductor—a vein solution, for example—in which the current would consist in the migration of cations upward and of anions downward. Practically every kind of solution could function to some extent at either one end or the other of the cell suggested. Cathodic effects, such as those described, would occur chiefly at the upper levels; anodic effects would predominate at the lower levels.

By such "chemical action at a distance"²² it would seem that the oxidizing and reducing zones would be expended either in one direction or the other somewhat faster and possibly further than by diffusion alone.²³ As a matter of fact, the process should probably be conceived not as extending from a given point to a remote point but as creeping along veins by local action, producing an extended zone at an intermediate stage of oxidation or reduction.

In the action suggested above the prime mover, of course, is the ferric sulphate produced by the oxidizing power of the atmosphere, and this oxidizing power of the surface solution is available through electric action at points in front of or below the oxidizing solution. In the same way a reducing solution at depth could exert an influence above it through electric action. As coming events cast their shadows before, a solution of sodium sulphide rising through a metalliferous vein system would by electric action tend to precipitate gold, silver, and copper on the minerals above. Of course, there would be a limit to the extent of either action, a limit set by a lack of proper electric circuits and by polarization, but the essential point is that electric action may cause "chemical action at a distance."

DEPOSITION OF ORES.

Ores are doubtless formed in a great many ways. Some sulphides appear to have been segregated during periods of igneous activity; others occur where obviously there was no igneous activity. In all the varied changes to which the compounds of the valuable metals are subjected fractional solution and precipitation seem to predominate.

According to Lindgren²⁴ the chief causes that produce ore precipitation from aqueous solutions are (1) mingling with other waters and (2) reducing agents. It is in the course of these changes that electric activity becomes a factor demanding consideration. One way in which electric action may effect at least ore solutions, and presumably the deposition of ores, by equalizing chemical differences along veins has been mentioned. Another effect of electric activity would be to keep the ores in a polarized state. The citation of known facts to explain the deposition of sulphides must necessarily be conjoined with qualifications due to uncertainty about the solutions. In general, however, the phenomena of deposition would probably be the reverse of those of solution. Other things being equal, an electric potential at which one mineral would be stable might differ from that at which another mineral would be stable. The several sulphides are by no means equally precipitable from solutions containing two or more metallic salts, and though that fact has heretofore been ascribed wholly to specific differences in solubility, there may be reciprocal relations between the electro-affinities of the metals and their precipitation by a sulphide which should be elucidated.

In considering the protection from chemical action afforded by electric polarization, it may be recalled that some metals are rendered "passive" by making them anodes for a short time. Similarly, the polarization of sulphides by positive electrification would undoubtedly preserve them by maintaining around them a film of hydrogen sulphide.

With a large current almost any metal may be plated out on sulphides; with a smaller current and potential, however, a sulphide may be formed instead of the free metal, just as a forced electrolysis of an acid or of an alkali salt with a mineral sulphide electrode evolves hydrogen, whereas a feeble current generates a soluble sulphide. Even feeble currents ordinarily precipitate only free gold or silver, but the slow precipitation of copper on even pyrite might produce some cuprous sul-

²² Ostwald, Wilhelm, *Das Chemometer: Zeitschr. physikal. Chemie*, vol. 15, p. 399, 1894.

²³ Percolation is entirely another matter and may be fast or slow according to the geologic structure. The electric effects must be of approximately the same order as those of diffusion, yet they may be superposed on diffusion effects and also may set up a selective diffusion of certain ions.

²⁴ Lindgren, Waldemar, *Econ. Geology*, vol. 1, p. 40, 1905.

* An Abstract from *Bulletin 548, of the U. S. Geological Survey*.

phide. So far, however, cuprous sulphide has not been produced electrolytically under conditions that would afford unquestionable results. In the electrodeposition of copper for analytical purposes, in the presence of sulphates, the copper is sometimes tarnished by sulphide, but it is doubtful whether this observation is applicable in a theory of ore deposition. If, however, electric currents might direct metallic ions toward the conducting sulphides, the metathetical reactions which would then occur are clearly indicated by Schürmann's series.²⁵ The suspicion that electric factors are not wholly negligible, even in metathetical reactions involving metallic ions, is greatly strengthened by the fact that there is a rough parallelism between Schürmann's series and the "electrolytic potential" series of the metals to be considered below. At present, however, there are absolutely no data on the subject.

More definite statements can be made about the metals than about the sulphides, as their behavior has been shown by many experiments in electroanalysis and related chemical processes. From a mixture of metallic salts in solution the metal of lowest solution tension will tend to deposit first in electrolysis, in accordance with the well-known "deposition potentials." The following table of electrolytic potentials gives the value assumed by the metal in a solution normal with respect to the metallic ion:²⁶

Electrolytic potentials.			
Au +1.356	Sb +0.743	H +0.277	Tl -0.045
Pt +1.140	Bi +0.688	Pb +0.129	Fe -0.063
Pd +1.066	As +0.570	Sn +0.085	Cd -0.143
Ag +1.048	Cu +0.608	Ni +0.049	Zn -0.493
Hg +1.027		Co +0.045	Mn -0.798

Some of the above values have been changed from time to time as better determinations of the ionic concentrations have been made, the latest value for silver being 1.06 volts, and for gold, about 1.8.²⁷

It will be noticed that gold, platinum, palladium, silver, and mercury show higher potentials in normal solutions of their respective ions than most of the minerals that have been studied show in salt solutions. Therefore, in cells constructed as follows:

+Metal / metal solution / potassium chloride / conducting minerals -

these metals deposit spontaneously until polarization puts a stop to the action. In such a cell the mineral is oxidized simultaneously with the deposition of the gold, silver, or other metal. In speculating on the starting of such action in nature it may be noted that most specimens not only have "points of weakness" but that in nature several sulphides are likely to be in association so that deposition seems likely to start unequally. No specimens of commercial iron and steel are so uniform throughout in composition or texture that some local electric action does not occur when they are immersed in solution.²⁸ In such specimens there are always some points of greater "solution tension" than others. We may, perhaps, assume that ores will also vary somewhat in structure or composition. When deposition has started, the metal deposited is very likely to serve as cathode for the deposition of more, and the principal factor limiting electric action is then the polarizability of the oxidizing sulphide. In this way the natural occurrence of filaments and nuggets may be very readily explained as due to electrodeposition in which the oxidation of a mineral more or less removed from the metal, if only still connected by the thinnest metallic thread, is an essential part of the process. That silver deposited by electrolysis is prone to form beautiful crystals is well known, although I am not aware that gold crystals have been so produced in the laboratory. I have observed nuggets of gold, however, which possessed a crystalline "treelike" structure exactly like that so well manifested by silver.

SOLUTION OF ORES.

The solution of ores may be the result of many different chemical agencies, but the facts indicate that electric action may be one of the factors where conducting minerals are present. The evidence afforded by experiment shows that a current passing from mineral to solution will produce oxidation—of the solution first if it is oxidizable, otherwise of the mineral. Alkali sulphides would go first, then alkali hydrosulphides, if present, and finally the ores, if no further reducing agents were present in the solution. Of several ores, the one of lowest potential would tend to be oxidized first.

Electrochemists are familiar with a class of feeble currents known as "residual currents." For example, the application of a low electromotive force to the electrolysis of water with platinum electrodes soon "polar-

izes" the electrodes with hydrogen and oxygen; further current flows only as fast as the gases dissolve in the solution and diffuse out of it into the air. The disappearance of an unstable mineral might be the supposed ultimate result of electric action between two or more ores, but practically this would occur very slowly on account of the accumulation of certain products of the reaction; in short, an equilibrium would be attained which would by no means be incompatible with the existence of two or more minerals. The disappearance of one would require a very long continued supply of fresh solution and the removal of the solution products. Specially rapid action, however, would be developed by the alternate drying and wetting of particles of different ores in contact. Traces of ferric salts that would form on iron minerals when dry would exert high potentials when moistened.

It is hardly necessary to point out that the order of solution of metals under electric action would be the opposite of the order of their precipitation—that is, when in contact the base metals would oxidize and dissolve first, then copper before silver, and finally silver before gold. Speaking broadly, the base metals would also protect most sulphides from oxidation if in contact with them in the presence of water, and the sulphides would protect silver and gold. Native silver and gold, as we now find them, may, therefore, have been held in their present position for a long time partly by the presence of sulphides which have now just about disappeared.

To summarize the electric activity of ores very briefly: Contact with solutions as well as certain other conditions impart electric potentials to conducting minerals. When local or electrolytic action is possible the chemical and electric differences will proceed toward equalization by processes of diffusion, decomposition, solution, oxidation, and reduction until the system reaches electrochemical equilibrium. Measurements of potentials are helpful in indicating the direction of possible changes and in giving a quantitative statement of the intensity by which the differences tend to become equalized.

SUMMARY.

A large number of metalliferous minerals are capable of conducting electricity and could, therefore, function as electrodes and as conductors for electric currents in ore deposits. In this paper only bare mention has been made of the possible existence of induced earth currents and thermoelectric currents, inasmuch as the field results of Barus on this point were almost wholly negative. It has been shown, however, that the energy which ordinarily manifests itself in chemical reactions may be, and in fact will be, manifested to some extent in electric action whenever the proper circuits are present. Conditions for electric action in ore deposits are by no means unusual. One of the simplest possible combinations by which electric action could occur would consist in the presence of two different active solutions in contact with a single body of ore, the two active solutions being united by any "indifferent" electrolyte. The combination suggested would have many ramifying variations, depending on the amounts of solution available, the position of the ores, and other like factors. The effects of electric action are naturally somewhat different from those which would result from direct admixture of solutions and entirely different mineral associations might be produced through such action.

The chemical difference producing the largest electric effects appears to be that existing between oxidizing and reducing solutions. All solutions may be arranged in an electromotive series grading, speaking broadly, from the strongest oxidizing solutions, which will charge an unattackable electrode most positively, to the strongest reducing solutions, which will charge it most negatively. It has been found that pyrite, and, to a less extent, several other minerals, are so inert to many solutions as to function electrically like "unattackable" electrodes for long periods, thus making oxidizing or reducing solutions available for producing electric currents in ore deposits. The solution products of minerals themselves may take part in producing currents in the absence of more active substances; accordingly, different minerals show different electromotive forces in "water."

The currents generated in any of these ways may cause effects at more or less remote points. Electric action on a large scale would tend to maintain a common level of oxidation along veins and large bodies of ore; where it is effective, the zones of oxidation and reduction would depend on the structure of the ore rather than on depth. Electric action on a small scale would polarize ores feebly, favoring the disappearance of unstable ores and protecting stable ores up to the point of equilibrium. The cathodic and anodic phenomena attending the passages of a current from a solution to a mineral, or *vice versa*, have been studied in some detail. It has been found that mineral electrodes possess various degrees of polarizability. The polarization of minerals would doubtless to some extent influence metathetical reactions in ore deposits. Feeble currents might also give a directional trend to metallic ions that would carry them toward the stable minerals. Under many conditions the valuable metals

would be deposited from solutions by electrolytic action and they would thereafter be protected from redissolving by contact with any of the more oxidizable ores.

A New Briquetting Material

A new binding material for making briquettes has been patented in France, consisting of 15 parts of glassmaker's sand, 18 parts Portland cement and 10 parts carbonate of soda, or other flux of silica, such as sea salt or sulphate of soda. From four to six per cent of this binder is mixed with the fine coal and coal dust, together with about eight per cent of water, and compounded in a mixer into which steam at about 16 pounds pressure and at a temperature of 170 deg. Cent. is admitted. This mixture is then pressed into briquettes. Heat may be applied as the blocks come from the press to increase the cohesion. This binder fuses to a vitreous mass at 200 deg. Cent.

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²⁵ For the latest discussion of the application of this series see Emmons, W. H., The enrichment of sulphide ores: U. S. Geol. Survey Bull. 529, 1913.

²⁶ Wilmore, N. T., Ueber Elektroden-Potentiale: Zeitschr. physikal. Chemie, vol. 35, p. 318, 1900.

²⁷ Abegg Handbuch der anorganischen chemie, vol. 2, pt. 1, pp. 674, 788, 1908.

²⁸ Cushman and Gardner, corrosion and preservation of iron and steel, p. 51, 1910.