

flies that for volatile solutes the osmotic pressure must be equal to the gaseous pressure corresponding to the same concentration. In this way the gaseous laws for the osmotic pressure can be shown to apply to volatile solutes, and, as most substances seem to be somewhat volatile, to substances in general.

Satisfactory direct measurements of the osmotic pressure have been made in a good many instances. But as those experimental determinations are very tedious, we rely more frequently on cognate phenomena—the depression of the freezing point and the lowering of the vapor pressure resulting in a solvent when some substance is dissolved in it. These depressions were found to be abnormally high in the case of electrolytic solutes, and this circumstance suggested to Arrhenius and Planck the idea of dissociation. For thermodynamically the osmotic pressure of dilute systems depends upon the number, and not upon the nature, of the particles; and when too high depression values were obtained, it would appear that we have not to deal with one particle of KCl, but with two particles—one of K and one Cl. The dissociation need not necessarily yield electrolytic ions, such as would call forth electric conductivity. Kahlenberg has observed pronounced dissociation in organic compounds dissolved in organic solvents which were nevertheless non-electrolytes.

The conductivity of a solution increases with the concentration, and decreases on dilution, while the equivalent conductivity increases with dilution and approaches on extreme dilution a constant value, corresponding apparently to complete dissociation. We have very few measurements at extreme dilution. The best freezing point determination by E. H. Griffiths gave 1.858 as molecular depression for cane sugar solutions; the gaseous value of the osmotic pressure would be 1.857. In the case of KCl, Griffiths found 3.720; twice 1.857 would be 3.714, so that here dissociation into two ions seems to be demonstrated. For binary compounds, the agreement is less good, and on these and other considerations are based attacks on the whole dissociation theory. Complex compounds are, however, possible even between monovalent elements; the halogens chlorine and iodine combine with one another, and in the alkali hydrides we have several atoms of metal or of hydrogen joined to one another. We must, therefore, not be surprised if the osmotic and dissociation laws do not strictly hold for all monovalent elements. Secondly, we must always bear in mind that the gaseous pressure law is only valid for very dilute systems, in which inter-ionic forces may be assumed to vanish. It must not be forgotten, finally, that in the determination of the coefficient of dissociation, the assumptions are commonly made that no complex ions are present, and that the ionic viscosity of the solvent is constant for all concentrations; both these assumptions are unjustified. We may imagine a non-dissociated molecule as a bipolar system; two molecules correspond to two magnets at great distance apart, and the mutual translational forces vary as the fourth power of the distance. In dissociated ions, on the other hand, we have isolated particles acting upon one another with forces varying as the square of the distance. These forces will hence remain active on dilutions at which the former forces, decreasing with the fourth power of the distance, no longer exert much influence. This, in Mr. Whetham's opinion, may be one of the reasons why the mass law and Ostwald's dilution law do not hold when good conductors like strong acids (in distinction from weak acids) are diluted.

Since chemical activity seems to depend much on ions, some electro-chemists have concluded that chemical action was possible only in the presence of ions. In that they have gone too far, and brought down sharp criticism on the whole theory. Kahlenberg has observed, e. g., that a precipitate of copper chloride is instantaneously produced when hydrochloric acid—itsself a non-electrolyte when absolutely dry—is passed into a non-conducting solution of copper oleate in benzene, and has for this reason, and on account of the behavior of solutions in other solvents but water, attacked the theory. We need not interpret these considerations in the sense that dilute solutions behave differently from concentrated solutions, and that the latter have to be treated again in a special way. The theory can fully account only for phenomena taking place under certain ideal conditions; under other conditions it affords a partial guidance. A considerable amount of experimental work on solutions in non-aqueous solvents has been collected within recent years, but the matter is not ripe yet for generalizations. To a certain extent the data are in accord with the dissociation theory; where they are not, we could hardly expect complete agreement. There are great experimental difficulties, and association of molecules often seems to take place in solvents like alcohols, acetone, pyridine, etc., and to complicate matters. That would not exclude the co-existence of ions, which could conduct the current in the modern sense. It is, further, not necessary that the many fused salts which are electrolytes are electrically dissociated. Osmotic data are not available, other experimental investigations are very difficult. Mr. Whetham points out that a fused salt consists of a collection of molecules all of the same kind, that hence arguments from the frequency of collisions between dissolved molecules, isolated from each other by comparatively vast spaces of solvent, cease to hold, and that there is, therefore, no real resemblance between the electrolyses of fused salts and of aqueous solutions.

It has been objected that thermodynamical deductions do not support the modern views as regards the theory

of the galvanic cell. Thermodynamics alone can in that case, however, not furnish any evidence either for or against any electrolytic or ionic hypothesis. But the simple concentration cell, in which the total potential difference is that due to the contact of two solutions of the same substance at different concentrations, can be explained by the hypothesis of independent ionic diffusion, as Nernst has shown theoretically and experimentally.

Attention may, in conclusion, be drawn to another circumstance. Since the development of the dissociation hypothesis as applied to liquid electrolytes, a vast increase has occurred in our knowledge of the discharge of electricity through gases. This process has been satisfactorily explained as a convective electrolytic action, the ions being in some cases dissociated molecules, in others isolated corpuscles which may represent the ultimate units of negative electricity, perhaps even the common constituents, aggregates of which make up the different chemical atoms. Such results give a presumption in favor of a general applicability of such theories. It is only a presumption. For, as Mr. Whetham points out, had the gaseous conduction phenomena been first in the field, we could not have extended a dissociation hypothesis, framed to explain them, to the much more complicated systems which are formed by electrolytic solutions. But for all solutions which conduct electricity the presumption in favor of a similarity of explanation is great. With this we must rest satisfied for the present, though we feel tempted to allude to catalytic processes. It looks as if two pure substances or elements were unable to act upon one another in the absence of some third body to start the reaction. That third body may, in pure water, be the ions to which the pure water owes that exceedingly small amount of conductivity which

in two ways: First, by means of a delicate electro-scope, such as is used in demonstrating electrical induction; and, second, by means of the sensitized photographic plate. With the first method, when a prepara-

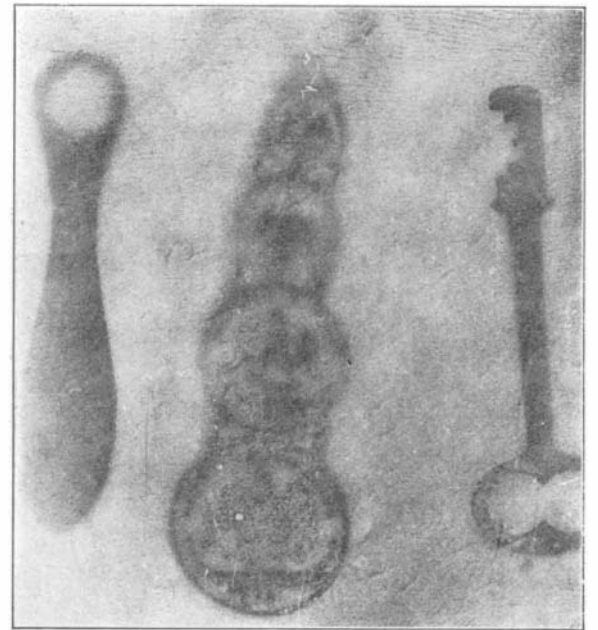


FIG. 2.—THORIOGRAPH TAKEN IN A DARK CLOSET BY OXIDE OF THORIUM SCREEN.

Time of exposure, 48 hours.

tion of thorium is brought near the wire attached to the two gold leaves in the electro-scope, the leaves fall together, thus indicating the presence of radioactivity. The greater the rate of the discharging power of the leaves, the greater the radioactivity.

The second test—that with the photographic plate—takes a much longer time for its accomplishment, viz., from twenty-four to forty-eight hours, if a screen made from the nitrate of thorium is used; but when hot emanations from the oxide of thorium are the excitant, a photograph may be obtained in one hour. Among the first thoriographs that I obtained was one taken by three Welsbach mantles. In a dark closet I placed a photographic plate. Upon this was laid a pair of scissors, as appears in Fig. 1, and on top thereof, three old Welsbach mantles, rich in thorium oxide. In seventy-two hours I obtained a good negative. In other thoriographs I have taken, I employed a screen of thorium oxide—using simply a piece of pasteboard—to which I added mucilage and dusted on it a thin layer of thorium. Thoriographs were taken by this method in from twenty-four to forty-eight hours. Figs. 2 and 3.

The most penetrating Becquerel rays are those obtained from hot thorium oxide. The thoriograph shown in Fig. 3 was obtained by taking a photographic plate, covering it with thick black paper, and placing on it keys, a glove buttoner, etc. Then this plate was exposed to the warm emanation of thorium, and the accompanying photograph was obtained in one hour.

The photographs that accompany this article—thoriographs I have called them—were produced by various methods and with varying degrees of exposure. The data concerning them will be found under each cut.

Prof. Ernest Rutherford, of McGill University, was among the first to investigate the properties of thorium. His researches in this field have done more, perhaps, than has been effected by anyone else toward solving some of the mysteries of this remarkable radioactive substance. In 1900 he discovered that tho-

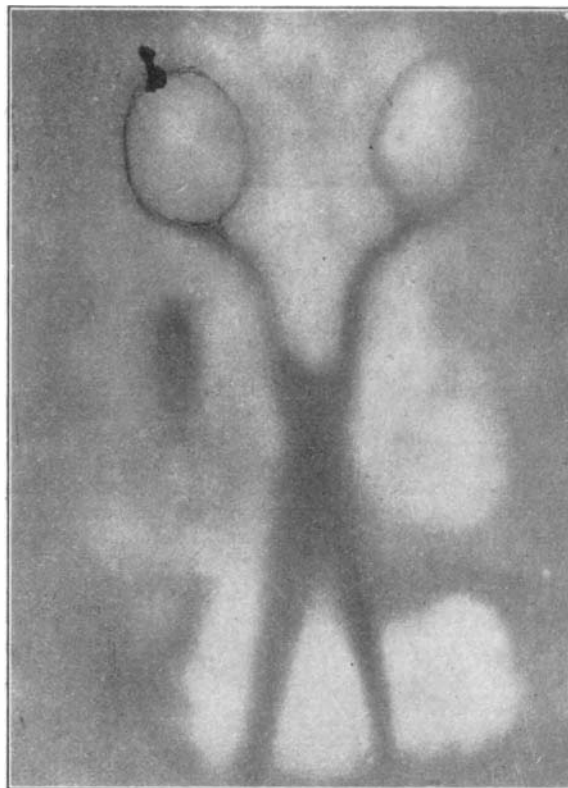


FIG. 1.—THORIOGRAPH TAKEN IN A DARK CLOSET WITH THREE BROKEN WELS-BACH MANTLES.

Time of exposure, 72 hours.

Kohlrausch has found it to possess. We do, of course, not wish to comprise all the varied catalytic phenomena under this point of view.—Engineering.

#### THORIUM: A RADIOACTIVE SUBSTANCE WITH THERAPEUTICAL POSSIBILITIES.\*

By SAMUEL G. TRACY, B.Sc., M.D., New York.

THE marvelous properties of radioactive substances have made them a matter of great interest to all scientists, but to the medical man their possible value as therapeutic agents renders them objects of special and peculiar importance.

There are but four known elements which are radioactive. These are radium, thorium, polonium, and actinium. The latter two I will not consider here, as they are the least known, extremely rare, and almost beyond the power of purchase. Radium I have already dwelt on in previous papers.† Thorium is one of the rare metals, and was discovered in 1828 by Berzelius. Until the past few years, it has been too rare and expensive to be used commercially or in medicine. It is now, however, more abundant, and is found in certain sands in North Carolina, in Brazil, and in Norway and Sweden. The most active thorium is obtained from the minerals cleveit, broggeri, monazite, in the order given. During the past ten years it has been used as the principal chemical for the production of incandescence in the Welsbach mantle.

Since the discovery of radium by Prof. and Mme. Curie, renewed interest has been excited in thorium, because it has been found, by Prof. G. C. Schmidt, to possess the property of radioactivity. That thorium is, in fact, radioactive, is susceptible of demonstration

\* From the Medical Record.

† New York Medical Journal, October 24, 1903; New York Journal of Advanced Therapeutics, December, 1903, and New York Medical Journal, January 9, 1904.

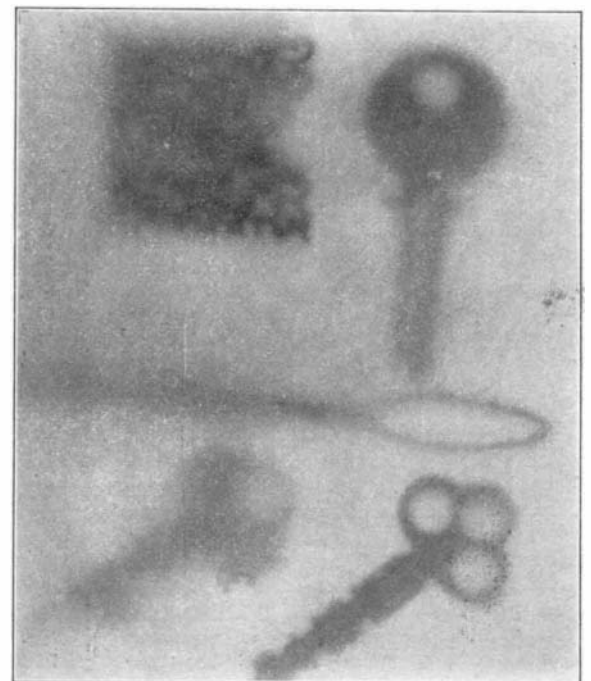


FIG. 3.—THORIOGRAPH TAKEN WITH THE EMANATIONS OF HOT THORIUM OXIDE.

Time of exposure, 1 hour.

rium gave off an inert and highly radioactive gas, which he termed an emanation. It diffuses through gases, liquids, and even through porous substances.

Rutherford considers the emanation to be the result of successive chemical changes in the thorium. By chemical action the thorium atom produces a substance which he calls thorium X, and by a further chemical change, this thorium X produces the emanation. The emanation expels from itself a negatively charged body, which constitutes the Becquerel rays. These rays are the same as those produced by radium, polonium, actinium, and uranium.

It has been recently proved by scientists who have experimented with thorium, that its radioactivity and emanations are antiseptic, antifermentative, and inimical to germ life. In conjunction with Hugo Lieber, we have shown that grape juice, when exposed to radioactive matter, will not ferment for a month, even though it is kept in a warm room, with the bottle uncorked. In other experiments the oils of juniper and erigeron were used. These oils ferment and decompose in a few days if left exposed to the light. But after treatment with thorium emanations, even in the presence of light, they nevertheless were preserved in their original state for several weeks.

The antifermentative property of thorium emanations is further shown by the following experiment:

Two bottles were taken, each containing agar-agar, starch, and mold (such as may be obtained from fermenting fruit). The contents of one of these bottles were subjected to the radioactive emanations of thorium, and those of the other were not. In the first bottle the growth of the mold was greatly inhibited, whereas, in the second bottle, the mold grew abundantly and soon filled the bottle. From these observations it is evident that thorium has a marked effect on micro-organisms and fermentation, a fact suggestive of a vast field of usefulness in medicine.

The radioactivity emanates from thorium in every form, whether in powder, solution, paste, or ointment. The best results, however, are likely to be obtained from the gaseous emanations when used as an inhalation. This form of emanation may be obtained, either by making a solution of thorium nitrate, or, better still, by heating the oxide in a glass receptacle, on a sand bath. For external application thorium may be made

of the emanations leaves in the lung cells a fine film of radioactive matter, which, in turn, produces the phenomenon of induced radioactivity in the same parts. This "induced" radioactivity will remain in the air-cells long after the original emanations have been exhaled. In most cases it lasts for from one to two days, after which it gradually disappears. In this connection it is interesting to observe that the radioactivity of thorium can be proved, even after it has entered the lungs. If a patient inhales the thorium emanations, and then, while in a dark room, exhales, allowing the breath to come in contact with a photographic plate, the exhalation affects, and partly decomposes, the silver salts on the plate.

As the induced radioactivity of the thorium emanations lasts from twenty-four to forty-eight hours, this acts as a guide to indicate the proper frequency for the treatments. An inhalation given every day or every other day would keep the lung cells constantly in a radioactive and antiseptic condition. While the thermometer in the Lieber apparatus should indicate a temperature of from 250 deg. to 300 deg. F., the emanations are partly cooled by passing through the glass and rubber tubing, and may not be much above the normal body temperature at the moment of inhalation. These inhalations may be taken for a period of fifteen minutes at the outset, which period may be gradually increased to half an hour.

This method of treating tuberculosis will not interfere with other measures, such as dietetic, hygienic, and even drug treatment.

#### CONDUCTIVITY OF DIELECTRIC LIQUIDS UNDER THE INFLUENCE OF THE RADIUM RAYS AND OF THE ROENTGEN RAYS.\*

From the French of M. P. CURIE.

I HAVE ascertained that the rays of radium and the Roentgen rays act on dielectric liquids as on the air, communicating to them a certain electric conductivity. The experiment is performed in this way: The liquid experimented with is placed in a metallic vessel,

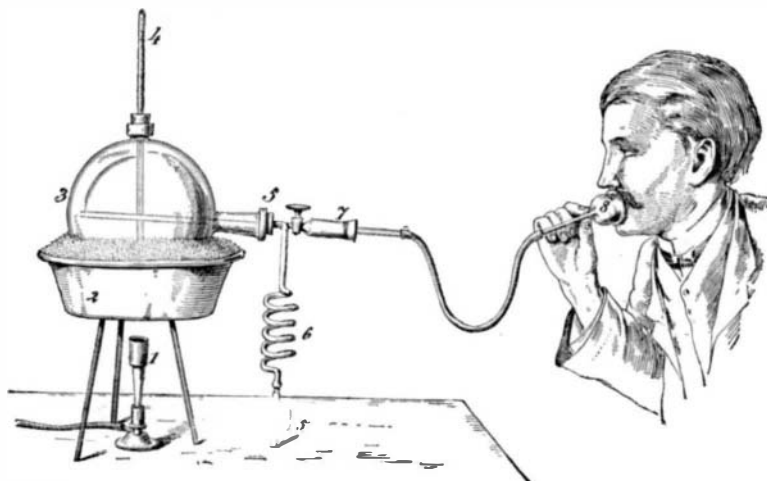


FIG. 4.—LIEBER'S APPARATUS FOR THORIUM INHALATIONS.

1. Bunsen burner. 2. Tin vessel containing white sand. 3. Glass vessel containing thorium oxide. 4. Thermometer. 5. Inlet for air. 6. Spiral glass tube to prevent escape of emanations. 7. Outlet for emanations. 8. Mouthpiece for inhalations.

into a paste or a 25 per cent ointment, and used as an antiseptic in chronic skin diseases, particularly those of parasitic origin.

Thorium in Tuberculosis.—Dr. Soddy, of London, and Prof. Rutherford, of Montreal, have suggested the use of thorium inhalations for tuberculosis. Certainly, from its antiseptic and antifermentative actions, it would appear to be a desirable agent to apply directly to the tissues affected in the fight against the tubercle bacillus.

As I have previously stated, there are two methods of obtaining these radioactive emanations, for use in the treatment of tuberculosis. One method is to use a saturated solution of nitrate of thorium in a large shallow receptacle. The larger the area of the vessel, the greater the amount of the emanations. A slight current of air can be caused to pass over the solution from a compressed air tank, while the patient is inhaling. With the nitrate of thorium there may be more or less free nitric acid; this must be neutralized by passing the emanations, before inhalation, through a wash-bottle containing a saturated solution of sodium bicarbonate.

The other, and by far the best, way of obtaining the emanations, is by heating the oxide of thorium. The apparatus I am using for this method of inhalation is the invention of Hugo Lieber. The accompanying cut shows the various parts of the apparatus, and the method of administering the thorium emanation.

The radioactivity of thorium is many thousand times less than that of pure radium, but thorium is also many thousand times cheaper (\$7 a pound), and it can be used for a longer period of time at each treatment, thus making up by the increased duration of the treatment what it lacks in potency.

Rutherford states that "when thorium nitrate is changed into an oxide by heat, it temporarily loses its radioactivity. However, when it is exposed to the air, it soon begins to regain its activity. In four days it is on a half and a half times more active; in twelve days, two and a half times; and at the end of two weeks it reaches its maximum radioactivity, which is four times as great as was the original nitrate of thorium."

In using Lieber's thorium apparatus, the inhalation

in which a thin copper tube is inserted. These two metallic pieces serve as electrodes. The vessel is kept at a given potential by means of a battery of small cells, of which one of the poles is earthed. The tube is connected with an electrometer. When a current traverses the liquid, the electrometer is kept at zero with the aid of a quartz piezo, which gives the measurement of the current. Another copper tube connected with the earth serves as a protection for preventing the passage of the current through the air. A bottle containing the radium-bearing salt is placed at the bottom of the first copper tube. The rays act on the liquid after passing through the glass of the bottle and the walls of the metallic tube. The radium will also act by placing the bottle beneath the vessel.

In order to act with the Roentgen rays they are introduced through the bottom of the vessel.

The increase of conductivity by the action of the radium, or the Roentgen rays, seems to be produced for all dielectric liquids; but in order to note this increase it is necessary that the conductivity peculiar to the liquid should be quite small in order not to conceal the effect of the rays. By operating with the radium and the Roentgen rays I have obtained results of the same order.

When the conductivity of the air or of another gas under the action of the Becquerel rays is studied with the same arrangement, it is found that the intensity of current increases proportionally with the difference of potential between the electrodes, when this difference of potential is slight, a few volts with the apparatus referred to; but when the difference of potential increases more and more, the intensity of the current no longer increases proportionally. The effect of an increase of tension goes on diminishing, and for high tensions (100 volts) the intensity of the current increases only to a small part of its value when the difference of the potential is doubled.

The liquids studied with the same apparatus and the same very radiant product behave differently. The current is proportional to the tension when this varies between 0 and 450 volts, even when the distance of the

electrodes does not exceed 6 millimeters. The conductivity occasioned in different liquids by the radiation of a radium salt acting under the same conditions may then be considered. The numbers of the following table, multiplied by 10<sup>-4</sup>, give the conductivity in ohms per cubic centimeter:

Carbon sulphide .....	20
Petroleum ether .....	15
Amylene .....	14.
Carbon chloride .....	8
Benzine .....	4
Liquid air .....	1.3
Vaseline oil .....	1.6

It may, however, be supposed that liquids and gases behave in a similar manner, but that for liquids the current remains proportional to the tension up to a much higher limit than for gases. The law of proportionality in the preceding series of experiments ceases to be verified only for tensions above 450 volts.

By analogy with what occurs for gases, the limit of proportionality may be lowered by employing a much weaker radiation. Experiment has verified this supposition. The product employed was one hundred and fifty times less active than that made use of in the first experiment. For tensions of 50, 100, 200, and 400 volts, I have obtained currents, which may be respectively represented by 109, 185, 255 and 335. The proportionality is no longer maintained, but the current still varies a great deal when the difference of potential is doubled.

Some of the liquids examined are nearly perfect insulators when sheltered from the action of the rays and kept at a constant temperature. Such are liquid air, petroleum ether, vaseline oil, and amylene. It is then quite easy to study the effect of the rays.

Vaseline oil is much less sensitive to the rays than petroleum ether. It is perhaps correct to refer this fact to the difference of volatility between these two hydrocarbons. Liquid air in a state of ebullition for some time in the experimental vessel is more sensitive to the action of the rays than that which has just been poured in. The conductivity produced by the rays is a quarter greater in the first instance.

I have studied the action of the rays on amylene and on petroleum ether at temperatures from +10 deg. to -17 deg. C. The conductivity due to the radiation becomes feebler by a tenth part only of its value when the temperature descends from +10 deg. to -17 deg.

In the experiments in which the temperature of the liquids has been varied, the radium can be kept either at the surrounding temperature, or carried to the same temperature as the liquid; the same result is obtained in both cases, from the fact that the radiation of radium does not vary with the temperature, and still preserves the same value even at the temperature of liquid air, as I have verified directly by measurement.

#### A CALORIMETER FOR COAL AND OIL.

It is of interest in the industries always to know with certainty the calorific capacity of any given variety of coal and oil, and for determining this there have been devised a certain number of calorimeters, the use of which, however, requires precautions and manipulations that are often very delicate. In many manufacturing there are laboratories in which all experiments that require a little care and study are performed, but such is not the case in the minor industries, in which simple and practical apparatus are indispensable. The want of such instruments is frequently the cause of expenses that might be avoided by manufacturers if they were provided therewith. It is evident that it is very important to know perfectly the quality of the coal employed, since coal that is well adapted for use in one case may prove inferior in another.

The calorimeter devised by Mr. Campbell Houston, of the Technical College of Glasgow, marks a progress in this line, and requires but a few manipulations, while the experiment proceeds under the eyes of the operator. The apparatus consists essentially of a large test-glass, which is filled with water into which is inserted a thermometer. The specimen of coal to be examined is reduced to powder in a mortar, and 30 grains of it are then put into a crucible, which is placed in a glass vessel that may be hermetically closed. This vessel is provided with an aperture to permit of the entrance into the interior of a tube for introducing oxygen taken from a reservoir. It is always well to employ the oxygen that is sold in the market in special cylinders. It may be manufactured upon the spot, but that is a complication.

After the powder has been put into the closed vessel, the latter is placed in the test-glass, into which has previously been poured two quarts of water, that is to say, a weight of about four pounds. The temperature indicated by the thermometer having been noted, the current of oxygen is allowed to enter, and the coal begins to burn. The entrance of the oxygen is regulated by a valve placed at the outlet of the cylinder containing the gas. At the beginning of the experiment, the extremity of the tube should be at the upper part of the vessel, and afterward be gradually and gently made to enter the interior until it reaches the lower part, at the end of the experiment, the duration of which is about ten minutes. After the combustion has terminated, the current of oxygen is maintained for a few seconds, and then interrupted. Then, after the water has been well stirred, in order that it shall be of the same temperature in all its parts, the graduation of the thermometer is read. The operator has now all the data necessary for the determination of the calorific power of the specimen submitted to exper-

\* Paper presented to the Academy of Sciences.