

Mekong; Mr. W. H. Cozens-Hardy, on surveys and research in Montenegro; and Mr. E. J. L. Berkeley, on British East Africa. It is also hoped that the Prince of Monaco, Sir Archibald Geikie, and Mr. J. Y. Buchanan may contribute papers. If Mr. and Mrs. Bent return in time from their projected exploring journey in Hadramant, an account of their work will be looked forward to before the close of the session.

A NUMBER of the *Journal* of the Manchester Geographical Society just issued (January to June, 1893) contains a paper on the Yoruba country, Abeokuta, and Lagos, by the Rev. J. T. F. Halligey, which gives some vivid descriptions of native life and manners.

DR. GERHARD SCHOTT'S physical observations on a voyage in a sailing ship from Hamburg to the China coast and back are published as an *Ergänzungsheft* of *Petermanns Mitteilungen*. In the discussion of his work Dr. Schott takes account of previous researches on the parts of the ocean he traversed, and his paper is an interesting addition to our knowledge of oceanography. The memoir is divided into two parts: hydrography, including a discussion of surface temperature as affected by diurnal range, rainfall, and wind, the specific gravity of surface water, surface currents and drifts, and observations on waves; and meteorology, dealing with the instruments employed, the record of air-temperature, humidity, and cloudiness. The memoir is, of course, well illustrated by maps and diagrams.

THE THICKNESS AND ELECTRICAL CONDUCTIVITY OF THIN LIQUID FILMS.

IN August, 1883, an article was published in *NATURE* (vol. xxviii. p. 389), signed by Prof. Rücker and myself, giving an account up to date of our researches on liquid films. Since that time our work has from time to time as opportunity offered been continued and further results have been obtained, a brief account summarise the results to which attention was drawn in 1883.

of which I now propose to give. It may be useful first to briefly A cylindrical soap film when allowed to thin under the action of gravity shows in succession the tints of the various orders of Newton's Colours, and finally becomes black. The thickness of any part of the film may be determined (supposing the refractive index to be known) from the colour it exhibits when light is reflected from it at a definite angle. The mean thickness of a horizontal ring of the cylindrical film may also be determined by measuring the electrical resistance of the ring, and by assuming the specific conductivity of the film to be the same as that of the liquid in mass. In the case of a liquid consisting of a mixture of soap solution and glycerine with a little potassium nitrate added to increase the conductivity, we proved by comparing the thickness of a film obtained by the optical method with the thickness deduced from its electrical resistance, that down to a thickness of $374 \mu\mu$ (micromillimetres)—corresponding to colours of the second order of Newton's scale—the specific conductivity of the liquid remains unaltered. When the film becomes thinner than $374 \mu\mu$, and exhibits the colours of the first order, estimates of its thickness derived from colour observations are less trustworthy, and when these colours are replaced by black, we only know from the colour that the thickness of the film has less than a certain maximum value. Assuming, however, the specific resistance to be unchanged when the film became black we showed that the thickness of such a black film does not differ much from $12 \mu\mu$.

Experiments were then carried out by the electrical method on a solution of oleate of soda (hard soap) containing 3 per cent. of KNO_3 but no glycerine. Black films made of this solution were found to have a mean thickness of $11.7 \mu\mu$, showing that the thickness of the black is practically the same whether the solution does or does not contain glycerine. As this result, however, depends upon the validity of the assumption that the specific resistance of a black film is the same as that of a large quantity of the liquid, it was desirable if possible to measure the thickness in question by a method free from the assumption involved in the electrical method. For this purpose an optical method depending upon interference phenomena (*Phil. Trans.* 1883, p. 652) was employed. Two glass tubes about 16 inches long and $\frac{3}{8}$ inch in diameter were placed horizontally side by side and were traversed by two interfering beams of light, the interference bands being produced by thick glass plates. The tubes were filled with plane soap films, each tube containing from 40 to 60 films and having its ends closed by pieces of plate-glass. After an hour or

more, when the films had thinned sufficiently to appear black, the position of the central interference band in the field was noted, and its displacement when the films were broken, first in one tube and then in the other, carefully measured. From these measurements the average thickness of a black film could be easily deduced, the only assumption made being that the refractive index of the liquid is unaltered by the tenuity of the film. The average thickness of about 900 films was found to be $12.1 \mu\mu$. This result justified the assumption made in the electrical method with regard to the constancy of the specific conductivity of the liquid.

The results established before the recent work was begun were therefore as follows:—(a) The thickness of a black soap film formed of a solution containing one part of oleate of soda dissolved in 40 of water with 3 per cent. of KNO_3 added is about twelve micromillimetres. (b) It is practically the same when to the soap solution is added two-thirds of its volume of glycerine. (c) From this it follows that the specific conductivity of such a solution is the same whether the liquid be considered in large quantity or in the form of a minutely thin film. (d) The thickness of the black, though often varying from film to film, is always the same in the same film—*i.e.*, is independent of area and age. With regard to these results it may be said at once that they have all been repeatedly and completely confirmed by subsequent investigation.

We now come to the more recent work. Since in the earlier experiments the solutions were always of the same strength as regards soap, and always contained not less than 3 per cent. of KNO_3 , it was important to determine whether the thickness of a black film is or is not dependent upon the proportion of soap or salt in the solution. The optical method was first employed. The strength of the soap solution being kept constant, *viz.* 2 grammes of hard soap to 100 cc. of water, the proportion of salt was diminished from 3 per cent. to zero. Under these circumstances, the mean thickness of a black film was found to steadily increase from $12 \mu\mu$ to about $24 \mu\mu$. A similar large increase in the thickness was found when the solution contained glycerine, or was made of soft instead of hard soap. When no metallic salt is present, and the strength of the soap solution varies, the thickness of the black increases as the solution becomes more dilute. Thus for a hard soap solution, when the percentage of soap was 3.3, the thickness was found to be $21.6 \mu\mu$ and rose to $29.3 \mu\mu$ as the percentage of soap diminished to 1.25. If, on the other hand, the solution contains as much as 3 per cent. of KNO_3 , variation in the proportion of soap has little or no influence on the thickness of the black. This is shown by the following table:—

Hard Soap Solution, containing 3 per cent. of KNO_3 .							
Percentage of soap in the solution	2.5	...	2.0	...	1.66	...	1.14
Mean thickness of the black in $\mu\mu$	13.1	...	12.1	...	11.6	...	12.1

The results above given have been deduced from the optical method of measurement, and the question arises whether the large increase in the thickness of black films formed from an unsalted solution is real, or whether it is due to some incorrect assumption. The only point where error is possible is in the hypothesis that the refractive index is the same as that of the liquid in mass. The thickness of a film varies inversely as $\mu - 1$ (μ being the refractive index), and as the refractive index of the soap solution is 1.34, it would have to be reduced to 1.17 in order that the calculated thickness might be doubled. It appears therefore *à priori* extremely improbable that the mere addition of 3 per cent. of KNO_3 should so completely change the optical properties of the liquid that whereas if the salt be added the refractive index is practically the same in the thin films and in the liquid in mass, yet without the salt the refractive index should be as much as 13 per cent. less than that of the liquid in mass. It may further be mentioned that Drude (*Wied. Ann.* xliii. p. 169, 1891), by an optical method quite different from that employed by us, has compared the refractive indices of black and coloured films, of which the latter may unquestionably be taken as nearly if not quite identical with that of the liquid in mass, and has shown that they do not differ by more than 1 part in 140. Such a variation would not affect the apparent thickness of the films as measured by the optical method by more than 3 per cent., whereas, as we have seen, the presence or absence of the salt alters the apparent thickness by 100 per cent. On the whole, then, the evidence is very strong that the differences of thickness indicated by the optical method

are not merely apparent but real, and this point may now be treated as established.

We now pass on to consider the thicknesses of black films as deduced by the electrical method. The method adopted was in all essentials identical with that previously employed and described (Phil. Trans. 1883, pt. ii. p. 645, NATURE, 1883, *loc. cit.*).

The apparent thickness of a black soap film as measured by the electrical method increases as the percentage of added salt diminishes, but in a far larger ratio than would be inferred from the optical method. If the proportion of salt be diminished to zero the thicknesses thus calculated are greater than the greatest thickness at which a film can appear black. Thus with a hard soap solution the apparent thickness rose from $10.6 \mu\mu$ to $26.5 \mu\mu$, as the percentage of KNO_3 added was diminished from 3 to 0.5, and became $148 \mu\mu$ when the solution contained no salt, this number being the mean value derived from fourteen films, the individual thicknesses of which ranged from 79 to $240 \mu\mu$. In another set of experiments made with a rather stronger soap solution, the apparent mean thickness of the black was $184 \mu\mu$, the extreme values for six films being 84 and $250 \mu\mu$. Similar results were derived from a soft soap solution, the mean apparent thickness obtained from the examination of twenty-three black films being $162 \mu\mu$, and the extremes about the same as before, viz. 80 and 252.

Now a film $148 \mu\mu$ thick (to take the smallest of the mean thicknesses given above) could not possibly appear black. According to Newton the beginning of the black occurs when the thickness is $36 \mu\mu$, which is about one-fourth of the smallest mean value obtained from unsalted solutions. We are therefore driven to the conclusion that the close agreement between the results of the optical and electrical methods, which has again and again been proved when the solution contains 3 per cent. of KNO_3 , does not hold in the case of unsalted solutions. The measured thicknesses cannot be true thicknesses, and therefore there must be a difference between the specific conductivity of a film, and that of the liquid from which it is formed.

Apart from this, however, is the fact that the apparent thickness varies considerably from film to film, although all the conditions are maintained as far as possible constant. This is certainly due in some cases to a real variation in thickness. We have frequently seen in the same film two different shades of black separated from each other by a definite sharp line, which is generally very irregular in form. The line which separates the black from the coloured part of a cylindrical film thinning in the normal way is always a horizontal circle. This is rarely the case with the boundary between the two black tints. Sometimes a patch of the darker black is completely surrounded by the other, sometimes the line of separation is sinuous, or stands higher at one point than at another. It is thus difficult to obtain comparative measures of the thicknesses of the two tints, as the method of experiment employed assumes the thickness of a cylindrical film to be the same at all points on the same horizontal circle. Such measures, however, as have been made indicate that the thickness of the thicker black is about twice as great as that of the thinner.

The two black tints are not always easy to detect or to distinguish from each other. If only one occurs it is almost impossible to say whether it is the thinner or thicker variety. Frequently the passage of an electrical current through a film, the black portion of which appears to be homogeneous, discloses the existence of the two different tints by producing or intensifying little white flecks which lie along the boundary between the two. On the suppression of the current the flecks become smaller or disappear, but the attention of the observer having been called to the boundary line, there is no difficulty in distinguishing between the regions on the two sides of it, the thinner appearing more intensely black than the other. We have never, when experimenting with solutions containing 3 per cent. of KNO_3 , seen any indication of the two shades of black. If the added salt is reduced to 0.5 per cent., the phenomenon is seen occasionally; but with unsalted solutions it is of frequent occurrence. The two varieties of black in a soap film were noticed by Sir Isaac Newton, who remarks that sunlight is reflected from even the darker spots.

But to return to the question of the mean apparent thickness of a black film. As has been stated, the optically measured thickness differs little if at all from the true thickness. If the electrical thickness is approximately equal to the optical thickness, we may assume that the specific conductivity of the liquid

is unaltered by the tenuity of the film. If they differ considerably the inference is that the specific conductivity has changed. Now in the case of an unsalted solution containing one part of soap dissolved in sixty of water the optical thickness is $27.7 \mu\mu$, while the mean apparent electrical resistance is $160 \mu\mu$. The specific conductivity is therefore greater in the film than in the liquid in mass in the ratio of 5.8 to 1.

A number of experiments have been carried out for the purpose of determining whether the change in the specific conductivity is a function of the thickness of the film, or is peculiar to black films. The result is to show that with an unsalted solution of hard soap the change begins when the film is comparatively thick. Thus, the ratio of the electrical to the optical thickness (which measures the proportional increase of conductivity) is 1.66 when the film exhibits the green of the second order (thickness = $641 \mu\mu$); it is 1.98 at a thickness of $296 \mu\mu$, 4.47 at $97 \mu\mu$ (white of first order) and becomes 5.8 when the film is black.

When the solution contains 3 per cent. of KNO_3 we know that for the black films the conductivity is the same as for the liquid in bulk. That it remains constant under all circumstances is highly probable, though not absolutely certain.

We have now to inquire into the possible causes of the fact that a black film made of an unsalted soap solution appears to be about six times as great as it really is, or, in other words, that the specific conductivity of the film is six times as great as that of the liquid in mass. This increase might possibly be due to (1) evaporation or absorption of water by the film as it thins, (2) changes of temperature, (3) changes in the chemical constitution of the film by the electrolytic action of the current employed, (4) absorption of carbonic acid or of oxygen from the air. In considering these it must be borne in mind that our observations are based on a comparison between two solutions which differ from each other only by the addition to one of them of 3 per cent. of KNO_3 . If, therefore, the change in conductivity were ascribed to any one of these causes it would be necessary to assume not only that the cause was competent to produce the change, but that its efficiency was very greatly modified by the addition of the salt. It is extremely improbable that evaporation or absorption of water, changes of temperature, or absorption of carbonic acid (if occurring in the one liquid), would produce the enormous observed change in the conductivity, while they were inoperative in the case of the other. We have not, however, been satisfied with *à priori* considerations, but have experimentally examined each of these possible causes.

With regard to the first, it is sufficient to say that all the precautions which experience has shown to be efficient in securing constancy of composition in the case of *liquide glycérique*—a liquid much more susceptible to changes of composition, due to variations of hygrometric state, than plain soap solutions—have been taken. We may be perfectly sure that the change in conductivity is not due to the loss or gain of water by the film when thinning.

Experiments have been made at various temperatures between 17° and 27°C. , but there is nothing in the results obtained to indicate that the apparent thickness of the black either increases or diminishes as the temperature changes. Thus, to take four films out of many that might be selected, we have the following results:—

Temperature	18.7 ...	21 ...	21.1 ...	26.3
Apparent thickness of black film in pipe	171 ...	237 ...	201 ...	135

There is no doubt that the relatively small changes of temperature which occurred in our experiments are not the cause of the large increase in the apparent thickness of a black film.

But the observed result might be due to change in the composition of the liquid caused by the passage of an electric current through the film. The current employed to measure the resistance of the film is always a feeble one; but in order to produce a rapid thinning, we have frequently passed a current from a battery of 28 Leclanché cells down the film from the moment of its formation. Such a current, though probably never exceeding 100 microampères, is passed for a long time, and might conceivably affect the specific conductivity of the liquid. As a specimen of the kind of results obtained, the following, derived from a soft soap solution, may be given. Each of the values of the thickness was obtained from a different film, and the number of cells indicated is that employed

to pass a continuous current through the film from its first formation. The measuring current was small and intermittent.

No. of cells.	Apparent thickness of black film, measured electrically, in $\mu\mu$.
0	150 171 148 150
14	155 145 142
28	150 157 179

The conclusion to be drawn from this table was confirmed by experiments in which transient currents from a Ruhmkorff induction coil were employed; they leave no doubt that the passage through a film of such electrical currents as we have used has no appreciable influence on the phenomenon under discussion.

To determine the possible influence of carbonic acid, or of oxygen, absorbed from the surrounding space comparative experiments were made. The apparatus not being air-tight, the plan was adopted of allowing a stream of air carefully freed from CO_2 , or of pure oxygen, as the case might be, to flow through the film-box. The results obtained under these conditions, though in some respects not quite satisfactory, justify the assertion that neither the total (or almost total) absence of CO_2 , nor a large increase in the quantity of oxygen in the neighbourhood of the film produces any appreciable change in the specific resistance.

It thus appears that a number of possible causes, to which the increase in the conductivity of a thin film might be due, prove on examination to have little or no influence. Although a satisfactory explanation is not at present possible, it will probably be found to depend upon the connection which subsists between the chemical constitution of a film and the surface forces which are brought into play, or are modified by its tenacity. Prof. J. J. Thomson ("Applications of Dynamics to Physics and Chemistry," p. 234) has drawn attention to this connection, and has shown that under certain conditions the chemical action in a thin film throughout which the forces producing capillary phenomena are active, may be totally different from the chemical action in the same substance in bulk. The experiment of Liebreich (*Berlin, Sitzungsberichte*, 1886) is often cited as illustrating this point. When solutions of chloralhydrate and sodium carbonate are mixed in suitable proportions in a glass tube, chloroform is slowly precipitated as an opaque cloud. Close to the surface, however, and from 1 to 3 mm. below the surface, there is a space perfectly clear and free from chloroform. It is supposed that in this space either the chemical action does not go on, or that if it does chloroform is not deposited. The explanation is not very satisfactory, and in any case the "dead space" is too large to justify us in referring it solely to the action of surface forces. Again, there is no doubt that the surface of a film becomes altered by the action upon it of the surrounding medium, so that the outer layers have different properties from the rest of the liquid. Lord Rayleigh has shown that the surface tension of a soap solution when the surface is new is nearly the same as that of pure water, but diminishes rapidly by exposure to the air. Reinold and Rucker have proved that the surface tension of a cylindrical film is increased by giving the film a new surface (letting fresh liquid flow over it) and that from ten to fifteen minutes elapse before the old value is regained. Other properties of the surface-layer besides its tension may be modified where it is very thin, and the electrical conductivity may be very different from that of the interior liquid. Although the peculiarities of the surface-layer certainly are in some way connected with the main facts here considered, we have shown that they cannot all of them be explained by the simple theory of the formation of a pellicle of different conductivity from the rest of the film.

It is difficult to assign a reason why the addition of salt to the liquid should produce so great a change in the results. In part, the better conducting salt probably masks effects which, when soap alone is used, become predominant; but it is likely that, in part at all events, it actually prevents the changes to which the change in conductivity is due.

The optical method of investigation illustrates the controlling influence of the metallic salt when present in the solution. As we saw above, a small variation in the proportion of dissolved soap has a large effect upon the thickness of the black when no salt is present; but the quantity of soap may be doubled without influencing the thickness, provided the solution contain 3 per cent. of salt.

A. W. REINOLD.

SPONTANEOUS COMBUSTION.

WHEN an inflammable substance ignites or becomes incandescent without the application of fire or other apparent cause, it has been customary to speak of it as spontaneous combustion, a term which I think I shall be able to show you presently does not correctly express the actions which lead to this apparently mysterious result.

Early in the eighteenth century a woman was found burnt to death under circumstances which gave no clue as to the cause of the accident, and in order to satisfactorily explain her death, the theory of spontaneous combustion was devised by the experts of the day, and was generally accepted at a time when little or nothing was known of what takes place during the process which we know as combustion; but as the years rolled on, men's views upon this important subject became wider and more exact, until, in the latter part of the last century, the great French philosopher Lavoisier, partly by his own experiments, and partly by the teachings of the work done by others, gave us a true knowledge of combustion and the changes which take place when a body is burnt, whilst the commencement of this century marked still further the advance of our knowledge in this direction, and also as to the conditions necessary for continuing the combustion or burning of any inflammable substance.

We now know that from the nature of combustion it is impossible for the human body to undergo spontaneous ignition or combustion in the way in which the novelists and scientific experts of the last century believed possible, but there are few amongst us who have not heard of, and even come across, cases in which large masses of coal, small quantities of oily rags, or waste, and hayricks which have been made from grass stacked before it was thoroughly dried, have ignited without any apparent cause, and have kept alive in our minds and on our tongues the term "spontaneous combustion"; and you must pardon me if I commence my lecture this evening by reviewing the teachings of Lavoisier's classical work, and then apply the conclusions we arrive at to those cases of spontaneous combustion which we meet with in our daily work.

The theory of combustion which was generally accepted during the last century, was that every combustible body contained within itself the products of combustion combined with a "something" called phlogiston, and when the substance was burnt, this phlogiston escaped, giving the flame or incandescence of combustion, whilst the products were set free. This theory could not, however, for long stand the test of exact experiment, and as soon as Black introduced the balance into scientific research, it was found that when any substance underwent combustion, the products weighed more than the body before it had been burnt, the reverse of what one would have expected had the phlogistic theory been correct.

During the last century lived Joseph Priestley, one of the most remarkable men this country has ever claimed as her own—a man so varied in his attainments, and so energetic in his life and labour, that he published over one hundred different works dealing with every conceivable subject, from theology to science; but it was in the latter field that he especially shone, and the greatest achievement of his life was the discovery of the gas which we now call oxygen, a discovery which he communicated to his friend Lavoisier.

Lavoisier at once saw the importance of the discovery which Priestley had made, and then conceived and carried out an experiment which has become historical as proving for the first time beyond doubt the fact that the air was not a simple elementary substance, but contained two perfectly distinct gases—oxygen and nitrogen.

Lavoisier placed in a long-necked retort about four ounces of mercury, and so arranged the apparatus that the air above the mercury in the retort should freely communicate with the air in a measured receiver, all contact with the outer air being prevented by standing the receiver in a vessel of mercury. He now heated the four ounces of mercury in the retort nearly to its boiling-point, and kept it at this temperature for twelve days and twelve nights. At first no change took place, some of the mercury merely distilling into the upper part of the apparatus and falling back again; but presently some little red specks began to appear on the surface of the metal, and increased in amount for several days, but at length ceased to form; and after continuing the heating for a day or two longer,

A lecture to working men, delivered by Prof. Vivian B. Lewes at Nottingham, in connection with the British Association