"On the Action exerted by certain Metals and other Substances on a Photographic Plate." By W. J. Russell, Ph.D., F.R.S., Lecturer on Chemistry at St. Bartholomew's Hospital.

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Having some years ago prepared for the purpose of spectroscopic examination several uranium compounds, it was of interest to make further use of them by repeating some of the very important experiments which Becquerel has made with these compounds. He has shown that if the metal or some of its salts be placed on a photographic plate in perfect darkness, and allowed to remain there for some days, the plate becomes acted on, the action being rendered evident by the ordinary photographic process of development. This action is readily produced, and belongs apparently to all the salts of this metal, and, as Becquerel has shown, to uranous as well as uranic salts. It is very remarkable that this power belongs also to the salts when in solution, and, as the action passes through glass, solutions of the double chloride or of the nitrate contained in a thin glass bottle, when placed on a photographic plate, act readily upon it. While speaking of these compounds it may be well to record some experiments which have been made to determine whether they lost their peculiar activity on being kept in the dark.

On the 10th August last, specimens of yellow oxide, recrystallised nitrate, and chloride, the latter in solution, were each divided into two equal portions, and all placed in similar clean thin glass bottles. One sample of each was then placed in total darkness, and the other kept in the light. These samples have from time to time been tested by placing them on a photographic plate for a week and then developing the plate in the usual manner. Seven such examinations have been made at about one month's interval. No very marked difference between the samples in the light and the dark has occurred; on the whole the samples preserved in the dark have proved slightly the most active, and this was decidedly the case with all three specimens at the last examination on March 26. Another experiment was begun a little later with the black oxide of uranium, which appears to be one of the most active of the uranium compounds; equal weights of a sample of this body were placed in two similar pill-boxes with a glass bottom; one has been kept in the dark, and the other in the light; after five months there was no difference in the effect which they produced on the photographic plate (Plate 2). The experiments are being continued. When repeating these different uranium experiments and using a card painted with the yellow oxide, perforated zinc was made use of simply as a screen to show the

activity of the uranium compound by the density of the picture of the pattern formed, but in place of obtaining in all instances a negative of the perforated zinc, *i.e.*, the action occurring where the plate was exposed, and none where covered by the zinc, the reverse took place, and the greatest amount of action occurred underneath the zinc. This happened over and over again, and even when the experiment was varied in different ways, so that the only explanation of the action was that the zinc itself must be able to effect a change of the same kind as the uranium, at all events, to act on a photographic plate, and further experiment with zinc alone proved this to be the case; later on it became known to me that R. Colson had already described this action of zinc in a paper in the 'Comptes Rendus' in January last, and had also found that similar results could be obtained with cadmium and with magnesium. He explains this remarkable action as due to vapour given off by these metals.

Both before and after seeing the account of Colson's work a large number of experiments have been made with zinc under different conditions, and there is no doubt of the ease and certainty with which the results can be obtained. The zinc, as Colson states, must be bright; if well rubbed with coarse sand-paper it is most active: probably this may, to some extent, arise from increase of surface; if cleaned with acid or with caustic alkali it is not so active, and zinc in its ordinary condition after exposure to the air ceases to be active. The salts also have no power of acting in this way. A polished piece of zinc laid on a highly sensitive photographic plate will, under certain conditions even in four or five hours, so act on it that on development a complete picture of the zinc is produced, showing the scratches or any ruled lines or faint pattern drawn on it, or if flaws in the metal exist they are clearly seen. A slight pattern produced on zinc by pressing on it a piece of white net and then rubbing it down with fine emery or sand-paper will give a picture in which the pattern is very evident. In fact, such a pattern forms a satisfactory test of this action of the zinc. Very slight alterations of the surface are shown in the picture. Absolute contact of metal and plate is not necessary. If screens of different thicknesses of any inactive substance be interposed between plate and metal, thus preventing contact, the action still occurs; if the screen be very thin, a picture of the zinc surface is still obtained, but if thicker, only a dark cloudy patch is formed. Still further, if a thick piece of glass tubing an inch long be placed on a photographic plate, and the upper end covered with a piece of polished zinc, in a week to a fortnight distinct action will be found to have taken place below the zinc. Since the action then is not one of mere contact, the next point was to ascertain whether it would be transmitted

through different solid or liquid media. Glass, even of the thinnest kind, was found to stop the action, but many other substances allow of its transmission. For instance, the action takes place readily through celluloid, sheet gelatine gutta-percha tissue, collodion, vegetable parchment, real parchment, gold-beater's skin, tracing paper, and no doubt many other bodies. With all these bodies experiments have been made by placing the medium first in contact with the zinc and the photographic plate, then by introducing a screen so as to prevent the medium from touching the zinc, and then placing a second screen so that neither zinc nor plate were in contact with the medium. The screens were made of different materials, most commonly of either white cardboard or sheet indiarubber, and of different thicknesses. The details of each experiment need not be here described, but the general results obtained are that with thin sheet gelatine, either red, green, or blue when laid on the zinc, the action readily passes through, and a good clear picture of the surface of the zinc is obtained, and even with two sheets of gelatine a similar effect is produced. With thick sheet gelatine interposed the action on the plate still takes place, but of course the exposure must be longer. Warm solutions of gelatine were painted on polished zinc and allowed to harden; the action took place through such layers as readily as through the films. With screens used as before described to prevent contact the gelatine still allowed the action to take place through it. Thin sheets of celluloid about 0·28 mm. in thickness allowed the action to take place through them, and sheets 0·81 mm. in thickness also allowed the action to be transmitted. Again, gutta-percha tissue was found to act in the same kind of way as the gelatine and celluloid. The other media experimented with, although possibly not so uniform and continuous in structure as the foregoing, also allow this action to be transmitted to them.

Gold-beater's skin and tracing paper both allow the action readily to pass through, and pictures of the zinc are readily obtained. If either of these bodies be placed between a piece of perforated zinc and the plate, the perforations are very distinctly shown, or if they be placed between a double screen with corresponding holes cut, a picture of the holes is readily obtained.

Both vegetable and real parchment are also transparent to this action, but not so much so as the previously-mentioned substances; the vegetable parchment is more transparent than real parchment. When in contact with the zinc a picture of the zinc surface is obtained, but this is somewhat modified by the substance of the parchment.

If different kinds of ordinary papers, such as writing and drawing papers, be interposed between polished zinc and a photographic

plate, interesting results are obtained, for the pictures formed show clearly the structure of the papers, and also show that papers have very different powers of transmitting this action. Certain writing papers are quite opaque to the action; with others pictures of the structure and the watermark are easily obtained.

The painting a paper with India ink does not destroy its transparency. Obviously pictures of bodies, such as skeleton leaves or dried flowers, &c., are easily obtained in this way.

A mere difference of colour does not appear to alter the absorptive power of a medium; at least, this is the case with gelatine. The thin sheets of gelatine, whether red, green, or blue, have no difference in their absorptive power, and when gelatine, coloured with aniline dyes, is painted on polished zinc, the colour does not affect the amount of action which takes place. The same thing happens if demy paper be painted with different coloured solutions of gelatine. With ordinary pigments different results are obtained, but these results need not be discussed on the present occasion.

In addition to the metals cadmium and magnesium, mentioned by M. Colson, there are certainly many others which are able to produce effects similar to that produced by zinc. There are also certain alloys which can act in the same way. The following is a rough list of active metallic bodies approximately in the order of their activity: mercury, magnesium, cadmium, zinc, nickel, aluminium, pewter, fusible metal, lead, bismuth, tin, cobalt, antimony.

The above order, even if not absolutely correct, is sufficiently so to indicate that, although mercury is the most active, the other metals do not follow in the order of their fusibility or exactly according to any obvious physical property, but most nearly according to their position in the electrical series. Mercury is, then, at ordinary temperatures the most active metal, and its action is exercised not only when the photographic plate is placed half an inch or so above the metal, but when gelatine, gutta-percha, tracing paper, vegetable parchment, are interposed. It appears, however, that the action of the mercury does not take place as readily through gelatine, but more readily through gutta-percha than is the case with zinc.

Magnesium is also a very active metal, and very good pictures, showing every scratch on its surface, are easily obtained; also very marked effects are produced when both single and double screens are used. Cadmium also produces very good pictures, and is rather more active than zinc; nickel and aluminium are not quite so active, but give good pictures; then follow lead, bismuth, and tin. The last metal is by far the least active. Only a few alloys have at present been experimented with; brass gives no action, but ordinary pewter, and fusible metal, consisting of lead, bismuth, and tin, were found to have considerable activity, and are placed in the

list between aluminium and lead. That certain alloys should act in the same way as the metals is certainly of interest, and probably of considerable importance. The oxide and sulphate, both of zinc and cadmium, were found to be devoid of any power of acting on the photographic plate. Iron, gold, and platinum, are not active, and copper only very slightly. All the above results are founded on experiments in which the exposure lasted for one week; with longer exposure other metals will probably produce some action.

In order to determine whether moisture was an active agent either directly by affecting the medium or indirectly by affecting the photographic plate, experiments were made by exposing the plates under bell-jars, in which in one case there was water, and in the other sulphuric acid or calcium chloride, and even in these extreme cases no appreciable difference was found to occur, and even if the membrane was purposely damped it did not appear to aid the action except by bringing it closer to the metal, so that aqueous vapour is not apparently an active agent in producing these reactions. In an atmosphere of hydrogen the action takes place as it does in air. Carbon dioxide, under ordinary conditions, does produce an effect, but this probably arises from its action on the zinc plate. Alteration of temperature produces very marked effects; increase the temperature, and the action of the zinc is greatly increased; for instance, two similar plates, both wrapped in tinfoil and the plates separated from the zinc by means of a cardboard frame. One was placed on a water bath and exposed to a temperature of about 70° C., and the other placed in a vessel of ice at 0° C. After five hours the one which had been exposed to the high temperature had given a black picture, while the one at the low temperature gave a picture barely visible. A similar experiment was also made with nickel, and this gave, after heating to about 70°, a good dark picture, but the corresponding experiment, when the metal was kept at 0° for five hours, gave no picture at all. Aluminium, when treated in the same way, gave at the higher temperature only a faint picture, but at the lower temperature, even after two days, no picture at all. It has already been mentioned that this action of the metals cannot pass through even thin glass, nor can it pass through selenite, nor a layer of gum arabic, nor one of paraffin. Glass being impervious to the action, renders it somewhat difficult to try satisfactorily the action exerted by liquids, but celluloid may be used for this purpose; also mercury may be covered with a thin layer of water, and then its action entirely ceases. The action of certain salts in the dry state has, however, been tried by soaking non-glazed paper in different solutions, drying it, and then placing it, either with or without a screen, between the zinc and the photographic plate. These experiments have given some interesting results; for instance, paper

soaked in the following solutions, alum, potassium chromate, zinc sulphate, and quinine sulphate, renders the paper quite opaque to the action of the zinc.

No doubt this action of alum accounts for certain papers not allowing the action to pass through them. Some singular developments of this subject have arisen from experiments made while examining the metals. A piece of polished zinc was coated with copal varnish with the object of ascertaining whether the action would take place through such a medium, and in case it did, as it was thought at the time, of demonstrating that the action could not arise from metal vapour. The experiment was quite successful; the photographic plate, notwithstanding the varnish, was strongly acted on. The experiment was repeated several times, and always with the same result; but the pictures seemed rather too good, darker than those given by the zinc alone, and on trying the copal on plain glass instead of on zinc it proved that effects apparently similar to those obtained with zinc were produced. What is known as picture copal answers very well for these experiments. That prepared by Winsor & Newton has been used. This is painted or poured on a clean, warm glass plate, and allowed to harden completely. The plate can then be used in the same way as the zinc plates. If a photographic plate be laid on the hardened varnish for two to seven days, a picture of the varnish, showing the streaks it happens to have dried in, is produced. If screens be interposed so as to prevent contact between the copal and the plate, the action still occurs, and, in fact, readily passes down a tube 1 inch long. Therefore, as with the zinc, any figure cut out in an inactive screen is readily produced on the photographic plate. Substances which are transparent or opaque to the action of the metals seem to act in the same way towards copal. It is rather more active than zinc. Glass is perfectly impervious to its action, but celluloid, gutta-percha tissue, and gelatine it permeates more readily than zinc does. The activity of the copal varies considerably under different conditions. If the powdered gum be sprinkled on a glass plate and then fused, it is not so active as when picture varnish is used. If the solid gum be dissolved in pure alcohol and ether, and applied to a glass plate as before described, it is far more active than after fusion. Heating it in a water bath for a considerable length of time certainly deprives it of a considerable amount of its activity; but this can be revived by wetting it with ether and allowing it again to dry at ordinary temperatures. As with zinc, increase of temperature increases its activity to a great extent. Experiments similar to those with zinc were made with copal. A coated glass was exposed to a heat of about 70°, and a similar one was kept at 0°. This one after five hours gave only a faint picture, whereas the heated one gave a dark picture, and a con-

siderable amount of action took place even through the cardboard screen. Many other bodies of the same nature as copal act in the same way. This has been proved to be the case with Damar and with Canada balsam, but copal seems to be the best representative of the class. Certain gums, such as gum arabic, gum senegal, have not the property of acting in this way. There are, however, a large number of bodies which have the power of acting in a manner similar to the copal; one of these is wood, and it possesses a very considerable amount of activity. Any ordinary smooth piece of wood laid on a photographic plate will act like zinc in impressing its picture on the plate.

A section of a young larch tree gave a good picture showing clearly the different rings and the layer of bark, which was the darkest part of the picture. The same section, when a film of gelatine was interposed between it and the plate, still gave a good picture. Wood which is thoroughly dried and hardened is also able to act in the same way.

A piece of mahogany 3·5 mm. thick, which had been in this form for at least thirty-five years and been carefully preserved in a dark cupboard, gave after a week's exposure a good picture, and the bottom of an old cigar-box acted equally well. Bodies such as straw, hay, bamboo, oiled silk, and, no doubt, many others, act in the same way. If wood, however, be painted with melted paraffin, it is no longer active. Ordinary charcoal also depicts itself on a photographic plate, but if it be heated for some hours in a covered crucible it loses this property. An ordinary piece of wood, if it be charred on one side by heating it with a Bunsen lamp, becomes remarkably active, as shown by placing it behind a screen with a pattern cut out. The action passes readily through different media, such as gelatine, tracing paper, &c., vegetable parchment, &c., and the structure of the charcoal is shown, when the action has taken place, even through a sheet of vegetable parchment. Coal and coke, sulphur, sugar, on the other hand, exert no action of this kind. When trying whether a copy of a lithographic picture could be obtained by placing behind it a plate of zinc, some curious results occurred. It would seem that printer's ink in most cases is not capable of acting, like copal, on a photographic plate, but that there are many cases in which it is a remarkably active substance. Specially so is the ink used in printing many of the newspapers. The 'Westminster Gazette,' for instance, is printed with an ink which very readily acts on a photographic plate. A portion of this paper with printing on only one side, laid with the blank side on the photographic plate, in a few days gives a remarkably black and distinct picture. If there be printing on both sides, then two pictures are obtained, the darker printing

becoming most evident on whichever side it may be. Interpose a sheet, for instance, of gold-beater's skin, and still the picture is obtained. The 'Standard' and 'Daily Graphic' are also very active, and the 'Times' only a little less so. The 'Evening News' is only slightly active, and the 'Morning Post,' 'Pall Mall,' 'Echo,' and 'Daily News' have not the property of acting in this way; at least, those copies experimented with had not. An admission ticket to the Society of Arts laid on a photographic plate, the ink away from the plate, also gave a very distinct picture.

Another singular case of an action of this kind was met with when experimenting with the uranium salts. Not having a sufficient number of small, clear glass bottles for a certain set of experiments, one of the compounds, the black oxide, was placed in a pill-box, believing that the action of the uranium would take place through the bottom of the box, and on developing the plate a dark circular space where it had stood was visible. The experiment was, therefore, considered very satisfactory, and, with different salts and for different objects, it was several times repeated. Ultimately it seemed evident that the uranium salts acted more strongly when in pill-boxes than in any other way, and on placing a pill-box without any uranium salt in it on a photographic plate it was found that action had occurred, as shown by the dark circular space produced.

The experiment was repeated over and over again, with the result that most pill-boxes have the power of acting on a photographic plate. Both new and old pill-boxes from different sources were experimented with, and almost all of them found to be active. There are, however, exceptions, and these, it was noticed, were always the more expensive and elaborate boxes. On examining the structure of a pill-box it was found that it is usually made of what is known as strawboard, covered with a thin white paper; on separately testing these two materials it was apparent that the white paper was without action on the plate, and that the strawboard was very active and produced exactly similar effects to those produced by the active pill-boxes. The inactive ones proved to be made of white cardboard, which is not an active substance. Samples of strawboard from several different sources have been tried, and all found to be active, and when separated from the photographic plate by means of screens, like the copal and the zinc, it gives a clear action. Different substances of a like nature have been tried, such as brown papers, &c. Some of them are more or less active, but none more so than common strawboard. Mr. Bevan was good enough to examine a piece of this active strawboard, but was unable to find any material other than straw present. Writing paper and, as mentioned before, white cardboard have not this power of acting on a photographic plate, but many kinds of brown paper

and no doubt many other bodies have the property. Many of the boxes in which photographic plates are packed are made of strawboard, but as the action does not pass through glass, the plates are but little or not at all acted on; but if a plate be laid face upwards in one of these boxes and left there for a week it will be very appreciably affected. If a small piece of glass be laid on the plate, it protects the film beneath, and shows clearly the amount of action which has occurred. If a box of this kind be painted inside with melted paraffin, this action does not take place. It happened that a few months before making the above experiments others were in progress in which black net was placed on a photographic plate simply to show clearly whether the plate had been acted on, and continually a reversed picture was obtained; this at the time could not be accounted for, but now the experiment was made of simply placing the black net on the photographic plate and leaving it there for some days; then on development a clear picture of the net was produced. The action is due to some material in the black dye, for white net does not act in the same way.

The action of the vapour from a few liquids on a sensitive plate has been tried. The plate was placed about half an inch above the liquid, and a screen, with holes cut in it, was fastened against the plate. Methylated spirit acted slightly on the plate; pure alcohol and ether had no action; benzene, coal-tar, crude wood spirit, linseed oil also, had no action, but turpentine and oil of cloves produced a slight amount of action.

Such, in outline, is an account of the experiments which have already been made on this subject. One point has led on to another, and some of the results were so unexpected that the experiments had to be repeated many times before full credence could be given to them. On the present occasion it is desired to do little more than record facts; further experiments, it is hoped, may lead to explanations not now evident. The supposition that all these active substances, the metals as well as organic bodies, give off a vapour capable of acting on a photographic plate, naturally suggests itself, and that copal does give off a vapour which directly or indirectly is active there can be no doubt. At the same time, it is at least difficult to suppose that the activity of such a body as strawboard should, after the treatment it has undergone, give off at ordinary temperatures sufficient vapour to produce the effects described, and the same applies to old dry wood, &c. Still more interest attaches to the action of the metals; do they emit a vapour so delicate in constitution and in such a quantity that it can readily permeate celluloid gelatine, &c., and produce a picture of the surface from whence it came, or is it a form of energy (possibly what has been called dark light) that these bodies emit? Zinc kept and polished in the dark

loses none of its activity. An experiment has been made with the object of reflecting the zinc action from glass. This did not succeed; whether this arose from the glass not being capable of effecting such a reflection, or whether a fortnight was not sufficient time to produce in this way a visible effect, is not known, but the experiment is being repeated. A photographic plate, suspended film upwards over a copal plate, was acted on round the edges in the way one would imagine a vapour to act. A similar experiment is being made over a zinc plate. The action of glass proves that there is at least a marked difference between the action exerted by metallic uranium and that by zinc and other metals.

It should be stated that it is only the most sensitive photographic plates which, without extremely long exposures, give the results described. The Mawson plate has generally been used in the foregoing experiments, but the Ilford special rapid plate acts equally well, and Edwards' isochromatic snap-shot plates are particularly sensitive to the action of the uranium salts. Lumière's extra rapid are not so sensitive as the Mawson and Ilford plates, and still less sensitive are the same firm's plates for yellow and green, and for red and yellow. Other sensitive plates have not been experimented with.

"On the Relative Behaviour of the H and K lines of the Spectrum of Calcium." By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S., and Mrs. HUGGINS. Received May 27,—Read June 17, 1897.

[PLATE 4.]

The remarkable relative behaviour of the lines in the spectra of certain substances as they appear at and near the sun's limb, and in the atmospheres of stars of different classes, has long been before our minds as a problem of great interest, which there is reason to believe is capable of solution by the methods of the laboratory, and on which we have worked from time to time for many years. Without waiting for the results of other researches which are in progress, we think that it is desirable to put on record some definite results on the behaviour of the lines of calcium, which appear to us to be conclusive, and of great importance in forming a correct interpretation of many solar and stellar phenomena.

As early as 1872, Professor Young from a few weeks' work at Sherman on the spectra of the chromosphere and of the prominences, was able to point out that "the selection of lines seems most capricious; one is taken and another is left, though belonging to the same element, of equal intensity, and close beside the first." Especially he noticed that while the H and K lines of calcium are almost always