

the body of a link may be as simple and easy to remember as possible, and bearing in mind that from circumstances connected with its manufacture the iron in the head of a link is perhaps never quite so well able to bear strain as that in the body, I think it desirable to have the size of the hole a little in excess, and accordingly for a 10" link I would make the pin  $6\frac{2}{3}$ " in diameter instead of  $6\frac{1}{2}$ ", that dimension being exactly two-thirds of the width of the body, which proportion may be taken to apply to every case.

As the strain upon the iron in the heads of a link is less direct than in its body, I think it right to have the sum of the widths of the iron on the two sides of the hole 10 per cent. greater than that of the body itself (see fig. 5).

As the pins, if solid, would be of a much larger section than is necessary to resist the effect of shearing, there would accrue some convenience, and a considerable saving in weight would be effected, by having them made hollow and of steel.

In conclusion, I would remark that my object in writing this paper has been, first, to call attention to the fact that a link is far more likely to be torn by the pin being too small, than a pin to be sheared by a link; and secondly, to try to establish a simple rule by which their proper comparative sizes may always be arrived at; and I have been induced to investigate this very important subject from having generally found in existing suspension-bridge chains a wide departure from what is right in this respect, in having the pins far too small.

III. "On the Influence of Quantity of Matter over Chemical Affinity, as shown in the formation of certain Double Chlorides and Oxalates." By GEORGE RAINEY, M.R.C.S., Lecturer on Microscopical Anatomy, and Demonstrator of Surgical Anatomy at St. Thomas's Hospital. Communicated by Dr. GLADSTONE. Received March 2, 1865.

The simple fact that quantity of matter has the effect of influencing chemical affinity is so well known and so generally admitted, that any special remark upon it would be superfluous; I shall therefore in this communication chiefly confine my observations to the compounds above named, by which this effect will be shown to be strikingly exemplified, offering such explanations and remarks thereon as the nature of the facts may seem to demand.

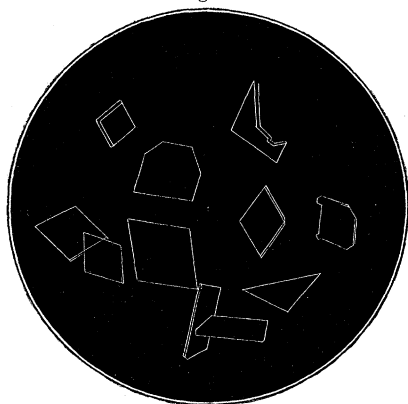
The results of nearly all the experiments mentioned in this paper were first arrived at by operating upon very minute quantities of material, and by observing under the microscope the changes that take place; but afterwards the same products were obtained on the large scale by appropriate processes, and in quantities sufficiently large to admit of being analyzed quantitatively, and of having their formulæ accurately determined. I shall therefore commence by giving an account of the processes by which the

various compounds I am about to treat of can be most easily prepared in minute quantities, and afterwards those by which they can be formed in any quantity that may be required.

All the apparatus necessary for the preparation of these compounds in quantities sufficient for microscopical examination, are a few cells made by cementing a ring of thin glass, such as is ordinarily used by microscopists, and some circular disks of thin glass to be employed as covers. The cell must be sufficiently shallow to allow of the examination of its contents with a lens of a half or quarter of an inch focus.

To prepare the compound of oxalate and chloride of strontium, introduce into a cell a few crystals of oxalate of strontia, and add to them as much saturated solution of chloride of strontium as will completely fill the cell; then cement upon the cell a thin glass cover in such a way that the cell shall be completely air-tight. A cell thus charged must be kept in a horizontal position, and examined from time to time. In a few hours the angles and edges of the oxalate of strontia crystals will be observed to have lost their sharpness of outline, being in a state of disintegration, and very minute crystals, altogether of a different form from those of the oxalate, to have made their appearance; and on successive examinations all the octahedral crystals will be seen to have disappeared, and to have become replaced by exceedingly well formed rhomboidal crystals of different sizes, composed of the two salts introduced into the cell. (Fig. 1.) In this ex-

Fig. 1.



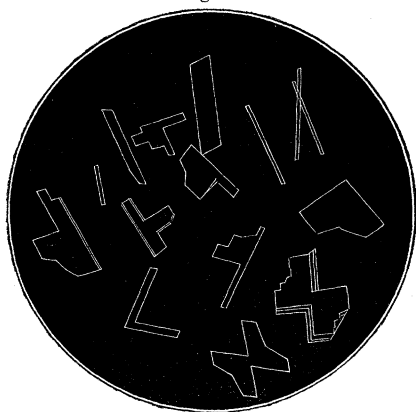
periment the solution of the chloride of strontium must be fully saturated; and if it even contain a few undissolved crystals, the processes of disintegration of the oxalate, and formation of the compound, will be prolonged, and more time allowed for their microscopical examination.

If, in the place of oxalate of strontia and chloride of strontium, crystals of oxalate of lime, and a strong solution of chloride of calcium be introduced into a microscope-cell, and the cell be closed up, the crystals of this oxalate (like those of the oxalate of strontia) will be seen by the microscope

to become gradually disintegrated, and replaced by an entirely different set of crystals, consisting of oxalate of lime and chloride of calcium. In this experiment, either the oxalate made artificially, or that obtained from any natural source, may be employed; but the strength of the solution of the chloride of calcium must not be less than that of a mixture consisting of equal parts by measure of a solution of this chloride saturated at a temperature of  $60^{\circ}$  Fahr. and water. The time required for the disintegration of all the oxalate of lime and its combination with the chloride of calcium to form crystals of the double compound of these salts, depends upon the size of the crystals of oxalate of lime employed in the experiment: if they are very small, or if the oxalate is to all appearance amorphous, evidence of these changes will be visible in a few hours, and the crystals completely formed in a few days; whilst if the oxalate crystals are large and well formed, some weeks will elapse before they have entirely disappeared and become replaced by the new crystals.

These changes are also influenced by the strength of the solution of the chloride of calcium: if it be fully saturated, they take place more quickly, but the crystals will be small; if diluted, they will, on the contrary, be produced more slowly, and the crystals will be larger and better defined. (fig. 2.) Crystals of oxalate of magnesia put into a cell with a saturated

Fig. 2.



solution of chloride of magnesium undergo similar changes, a double salt, consisting of oxalate of magnesium and chloride of magnesium, being formed. In this case the changes take place very slowly, several months being required for the formation of perfect crystals. These crystals have their sides and angles exceedingly sharp and well defined (fig. 3). Lastly, the oxalate of baryta, and a saturated solution of the chloride of barium placed under the conditions above mentioned, yield the same results, and crystals of oxalate of baryta and chloride of barium are formed (fig. 4.)

The series of facts requiring notice in the process of formation of these

double salts, as shown in the foregoing experiments, are, first, the disintegration, and at length complete dissolution of a class of salts of very

Fig. 3.

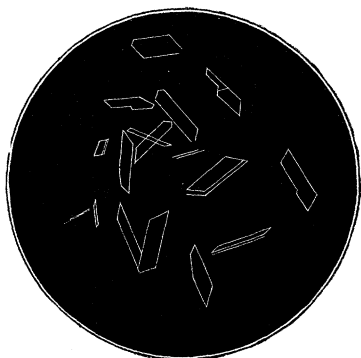
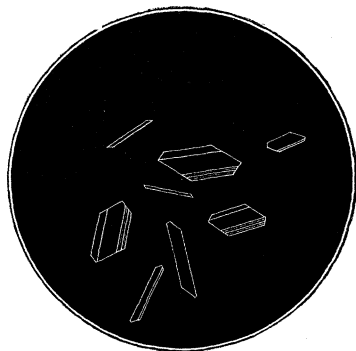


Fig. 4.



sparingly solubility, in strong solutions of chlorides of the same base, whilst weaker solutions do not in the least affect them; secondly, the combination under these circumstances of the oxalate and chloride of these bases to form double salts almost as little soluble as the simple oxalates; and lastly, the continued and simultaneous solution and deposition of these salts in a crystalline form in a quantity of fluid but little, if at all, exceeding the weight of the crystals deposited, until either all the oxalate crystals employed at the commencement are used up, or the solution of the chloride has become too feeble to effect the further disintegration of those which are in excess. The most remarkable part of this process is the continued deposition of crystals after the saturation of the fluid in which they were formed, rendering a small portion of fluid sufficient for the production of a comparatively large quantity of crystals. This fact seems to indicate that in this case the newly-formed particles, immediately on their coming into existence in this fluid medium, are attracted more forcibly by the fluid than by one another, but that afterwards, when they have become augmented to a point above that which is said to be the point of saturation, their attraction for one another becomes greater than that for the fluid with which they are in contact; and being thus brought within the sphere of action of the forces necessary to produce crystals, these particles combine into the crystalline form.

Whether under conditions like the above a deposition of crystals is a necessary attendant on the formation of sparingly soluble substances in a fluid medium, it is not possible to say; but in course of these investigations I shall be able to adduce several other examples of a similar kind.

The experiments which have been related so far have gone only to exemplify the influence of quantity of matter on chemical affinity as connected with simple chemical combination, but by a slight modification of

these experiments the effect of the same principle on elective affinity can be demonstrated. For this purpose let a small quantity of oxalate of lime, either amorphous or crystalline, be introduced into a microscope-cell filled with a completely saturated solution of chloride of strontium, and securely closed up. On examining such a preparation, the oxalate of lime is seen in a few days to be undergoing disintegration, and new crystals are seen to make their appearance, generally first at the sides of the cell. These crystals being formed slowly have a very sharp outline, and are remarkably transparent. In their form they resemble those obtained by putting oxalate of strontia into a saturated solution of the chloride of strontium; and notwithstanding that many of them have some of their angles cut off, and are thus made to present additional sides, their composition is precisely the same as if oxalate of strontia had in this instance been acted upon by a saturated solution of chloride of strontium. As in this experiment a chloride of calcium is formed at the expense of some of the chloride of strontium, the solution soon becomes too feeble to decompose the oxalate of lime, when of course the further formation of crystals will cease. Hence, to secure the best results, some crystals of chloride of strontium must be undissolved in the solution when put into the cell. By this means the processes of disintegration and the production of new crystals can be prolonged for many months, and an opportunity is thereby afforded of measuring them, and of determining their rates of increase, or of making such other observations on the subject as the experiment may suggest.

The methods of forming the double compounds of the oxalates and chlorides of the alkaline earths in microscopical quantities having thus been described, it now remains to show how, on the same principle, these compounds can be formed on the large scale.

To prepare the double salt consisting of oxalate of strontia and chloride of strontium, it is necessary merely to mix oxalate of strontia (made by decomposing the oxalate of ammonia by chloride of strontium, and washing the precipitate by decantation, and not on a filter) with a solution of chloride of strontium kept at the point of complete saturation. In order that no lumps of oxalate may be mixed with the solution of the chloride, which would be unavoidable if any portion of the oxalate had been allowed to get dry, it is necessary, after finally washing the oxalate, to draw off as much of the water as possible with a siphon, and to add to the mixture of the oxalate of strontia and remaining water the saturated solution of chloride of strontium containing some undissolved chloride. If the solution of the chloride of strontium in which the oxalate is contained is fully saturated, the combination will begin in a few hours; but it will require two or three weeks before all the oxalate has combined with the chloride. This can be determined only by the microscope.

The double salt of oxalate of lime and chloride of calcium can be formed in the same manner. In the formation of this compound it is not necessary that the solution of the chloride of calcium should be fully saturated; and

the weaker the solution of this chloride is, provided only it is of sufficient strength to combine with the oxalate, the larger will be the crystals of the double salt.

Since writing the above I find that the same double compound of oxalate of lime and chloride of calcium has been prepared by Fritsche by a different process.

Not having formed the double salts of oxalate of magnesia and oxalate of baryta with their respective chlorides on the larger scale, I am not able to give any special directions as to the easiest method of preparing them in large quantities; but from what has been stated concerning the microscopical processes, the mode of preparing them in such quantities is obvious.

Of the general properties of the double salt of oxalate and chloride of strontium, I may observe that it is very slightly soluble in the solution in which it is prepared, but rather more so in the hot than in the cold solution. It can be deprived in a great measure of the fluid in which it was formed, by pressure between sheets of blotting-paper: it is neither deliquescent nor efflorescent. It is decomposed by water into oxalate and chloride, but it is not at all affected by absolute alcohol, being entirely insoluble therein; hence this medium can be employed in freeing the salt from any adherent chloride: to effect this, the washing with absolute alcohol must be done by decantation, and not on a filter, as during the evaporation of the alcohol a small quantity of water is deposited from the air, which would decompose some of this compound salt, and, the chloride of strontium being soluble in alcohol, some oxalate would be left in excess.

For the analysis of this salt I am indebted to the kindness of Mr. Holmes, Dr. Gladstone's assistant, and Mr. Tribe of St. Thomas's Hospital.

The following is the formula deduced from the subjoined analysis of Mr. Holmes:—

$$\text{C}_2 \text{Sr}_2 \text{O}_4 \cdot 2\text{Sr Cl} \cdot 2\text{H}_2 \text{O} \cdot 4\text{Aq.}$$

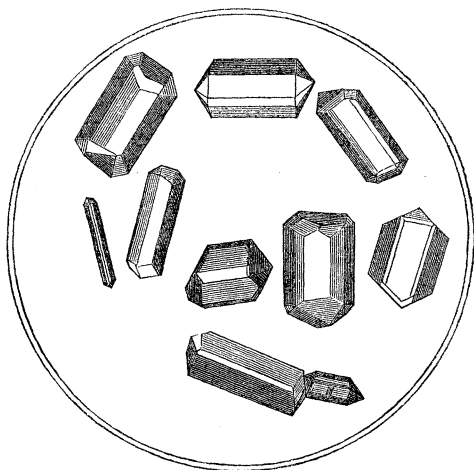
	Experiments. I.	II.	Theory.
Oxalate of strontium . . . . .	39·53	39·63	39·58
Chloride of strontium. . . . .	36·02	35·59	35·80
Water, fixed at 100° C. . . . .	8·11	8·25	8·18
Water, given off at 100° C. . .	16·34	16·53	16·44
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

which agrees with that deduced by Mr. Tribe.

Besides this there is another compound of oxalate of strontia and chloride of strontium, consisting of different proportions of these constituents, which can be prepared in the following manner:—To well-formed crystals of the above salt, contained in two or three times their weight of saturated solution of chloride of strontium, add gradually, and at intervals of two or three hours, a mixture of equal parts of saturated solution of chloride of strontium and water, until by examination with the microscope the greater

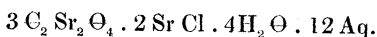
part of the rhomboidal forms are seen to have disappeared, and to have become changed into crystals of various sizes, and generally of a prismatic shape; after which the mixture is to be set aside for two or three days. If, after the expiration of this time, all the rhomboidal forms have not disappeared and become replaced by prisms, fresh solution must be added until such is the result. The size of the new crystals and their degree of completeness will be in proportion to the time employed in their formation. (Fig. 5 is a representation of these crystals.)

Fig. 5.



This compound of the double oxalate and chloride can also be prepared by keeping the rhomboidal form for three or four weeks in an atmosphere saturated with aqueous vapour, and completely excluded from the external air. By this mode of treatment these crystals in a few hours absorb water, and begin to undergo a process of disintegration, and in two or three days distinct well-defined prismatic crystals make their appearance. These processes of disintegration and formation of new crystals continue until all the rhombs are converted into prisms, which are contained in the water absorbed from the humid air, in which they may be preserved if kept in a well-stopped bottle, so as to prevent evaporation and the consequent re-conversion of the prisms into rhombs. This form of double salt, like the one from which it was prepared, is instantly decomposed, by the sudden addition of a sufficiently large quantity of water, into oxalate of strontia and chloride of strontium. It is not affected by exposure to the air, and it is insoluble in absolute alcohol.

The following is the formula deduced from the subjoined analysis by Mr. Holmes:—

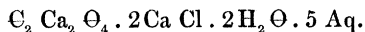


	Experiments. I.	II.	Theory.
Oxalate of strontium . . . . .	54·03	54·22	54·15
Chloride of strontium . . . . .	16·44	16·51	16·31
Water, fixed at 100° C. . . . .	7·77	7·40	7·39
Water, given off at 100° C. . .	21·76	21·87	22·15
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

With respect to the mode in which the change of the first compound into the second takes place under the circumstances above detailed, there is one fact which it is necessary to mention, namely, that the solution of chloride of strontium of the strength in which the prismatic crystals are formed from the rhomboidal, and in which they can be kept unchanged, does not affect the crystals of the simple oxalate. Hence it is evident that the oxalate set free by the decomposition of the rhomboidal crystals by the addition of only a small quantity of water, is, from the circumstance of its being brought into contact with the dissolved chloride of strontium on the instant of its formation, more easily acted upon by it than if it had before been in a perfectly formed state. This is probably from the nascent particles not having assumed a decidedly solid form; the chemical union would not require to be preceded by the same process of mechanical disintegration as in the latter case. The subsequent processes of solution of the incipient particles of the newly-formed salt, and their deposition in a crystalline form, admit of the same explanation as that already given in the case of the microscopic process.

As to the properties of the double salt of oxalate and chloride of calcium, I may observe that this salt is acted upon by water similarly to that of the oxalate and chloride of strontium, being instantly resolved into oxalate and chloride by the sudden action of water in sufficient quantity. The action of water applied gradually and in small quantity I have not sufficiently examined to be able to give a process for the preparation of a second salt. The salt is very slightly soluble in the solution in which it is formed, and rather more so in the hot than in the cold solution. After all the solution of chloride of calcium has been separated from it by means of blotting-paper, or by means of ablution with absolute alcohol, it is not deliquescent in an ordinary atmosphere.

The following is the formula deduced by Mr. Tribe from the subjoined analysis:—



	Experiments. I.	II.	Theory.
Calcium . . . . .	21·88	21·88	21·92
Oxalic acid . . . . .	23·67	23·67	24·11
Chlorine . . . . .	19·40	19·44	19·45
Water, fixed at 100° C. . . . .	10·36	10·14	9·86
Water, given off at 100° C. . .	24·69	24·74	24·66
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00



Before concluding this part of my subject, I have a few observations to make on the oxalates of the alkaline earths produced by the sudden action of water in sufficiently large quantity upon their double salts, especially those of the double salts of strontia and baryta.

For this purpose it is necessary only to drop a few well-formed crystals of the double salt of oxalate of strontia and chloride of strontium into a test-tube filled with distilled water, when they will be seen instantly to become opaque. The general form of these crystals remains more or less complete, but their interior is filled up with entirely amorphous oxalate, especially in the very thin crystals. If some of the crystals thus acted upon be put into distilled water in a microscope-cell perfectly closed to prevent the escape of the fluid by evaporation, and examined from time to time with a  $\frac{1}{4}$ -inch lens, they will be seen gradually to go into well-defined octahedral crystals, some months being required before the whole of the amorphous oxalate is converted into crystals; but all specimens thus prepared are not acted upon by water to the same degree. Among several slides showing this fact, I have one in my possession dated May 20th, 1863, in which the whole of the amorphous oxalate introduced has become transformed into remarkably beautiful and well-formed octahedral crystals, many of them of large size, considering that they had been formed in so small a quantity of water—the mere fraction of a drop. Some portions of this oxalate remained unchanged for more than a year after it was put into the cells, but the whole of it has since been converted into perfect crystals. As the effects of water upon these forms of oxalate are not uniform, it was considered necessary first to determine whether it was only on the oxalate as above prepared that water caused these changes, or whether it was not a general consequence of the action of water upon sparingly soluble salts, rendered amorphous in consequence either of a complete absence of water, or of an insufficiency for perfect crystallization (the sudden action of the water upon the double salt separating the chloride from the oxalate more rapidly than the water of crystallization could combine with it); and with this view the following experiments were performed. The oxalates of lime, strontia, and baryta, all made by precipitation in the usual way, were exposed, for the purpose of expelling the water of crystallization, in small test-tubes to the temperature of boiling oil for three or four hours, and afterwards put into closed microscope-cells with distilled water. On examination with the microscope, it was found that the oxalate of baryta had begun in a few hours to pass into a more minute state of division, and that on the same day octahedral crystals could be seen by a  $\frac{1}{4}$ -inch lens; and in the space of six weeks nearly all this oxalate had become transformed into regular octahedral crystals. The oxalate of strontia had undergone a similar change, but rather more slowly; distinct octahedral crystals, however, were visible in twelve hours.

As the oxalate of strontia obtained by precipitation in the usual way generally contains some octahedral crystals, some of the amorphous oxa-

late employed in this experiment had been prepared by exposing to the action of boiling oil an amorphous oxalate of strontia, precipitated from its combination with chloride by means of water. This precipitate not containing any octahedral crystals, and being acted upon more speedily by water than the other forms of anhydrous oxalate of strontia, is best suited for the demonstration of the effect above described. The oxalate of lime which had been subjected to the action of boiling oil and kept in distilled water had not undergone any visible change. I may notice, in reference to some oxalate of strontia which had been heated in boiling oil and exposed to the air for five or six weeks, that the action of water upon it was diminished, but was entirely restored after a second exposure to the heated oil.

In reference to the cause of these changes from the amorphous to the crystalline form by the mere action of water, it is evident that, as they take place in perfectly closed cells, and commence in so short a time after the introduction of the amorphous oxalate and water, they are independent of evaporation or of alteration of temperature. Hence they seem to be simply the effect of the chemical union of the water with the anhydrous oxalate to form a hydrous oxalate, which, being presented to the action of the water in the cell on the instant of its formation, is dissolved in a larger quantity than can be retained in solution, and thus whilst one portion of hydrous oxalate is being formed and dissolved, that which was formed previously is in the act of being deposited, and thus these processes go on simultaneously until all the amorphous oxalate which was introduced into the cell is changed into well-defined crystals, as was before explained in treating of the compound salt of the oxalate and chloride of strontium.

In conclusion I may add that the oxalates are not the only compounds of the alkaline earths which form double salts when brought into contact with strong solutions of chlorides of the same base. Crystals of tartrate of lime put into a saturated solution of chloride of calcium, form a double salt of tartrate and chloride of calcium, which is decomposed by water into tartrate of lime and chloride of calcium. Also the carbonate of lime, under favourable circumstances, will combine with the chloride of calcium to form a double salt which is acted upon by water, in the same manner as those above treated of. To obtain this last-named compound, it is necessary to put crystals of carbonate of soda or potash into a relatively large quantity of a saturated solution of chloride of calcium, so that the carbonate of lime, immediately on its coming into existence, may be acted upon by a solution of the requisite strength. Solid particles of carbonate of lime, whether crystalline or globular, are not affected by a saturated solution of chloride of calcium. Without doubt these experiments might be so modified and extended as to embrace other substances which are of very different degrees of solubility, and which still do not decompose one another; but as there is no apparent limit to such a course of experiments, I must now conclude my communication, hoping that the (in some respects)

novel method of chemical research which I have here exemplified may be considered of sufficient interest to be followed out by other investigators, and believing that the experiments and suggestions which I have here given, and the principles they involve, are calculated to throw some light on the nature of those chemical processes which take place in nature, whether in organized bodies or in the crust of the earth, neither of which branches of natural chemistry is at present sufficiently understood, and both of which it is of very high interest further to elucidate.

*April 6, 1865.*

Major-General SABINE, President, in the Chair.

The following communications were read:—

- I. "Report on the New Unit of Electrical Resistance proposed and issued by the Committee on Electrical Standards appointed in 1861 by the British Association." By FLEEMING JENKIN, Esq. Communicated by Professor A. W. WILLIAMSON. Received March 20, 1865.

Sir Humphry Davy, in 1821\*, published his researches proving a difference in the conducting-power of metals and the decrease of that power as their temperature rose. This quality of metals was examined by Snow Harris, Cumming, and E. Becquerel, whose table of conducting-powers, compiled by the aid of his differential galvanometer, and published in 1826†, is still frequently quoted, and is indeed remarkable as the result of experiments made before the publication by Ohm, in 1827‡, of the true mathematical theory of the galvanic circuit.

The idea of resistance as the property of a conductor was introduced by Ohm, who conceived the force of the battery overcoming the resistance of the conductors and producing the current as a result. Sir Humphry Davy, on the contrary, and other writers of his time, conceived the voltaic battery rather as continually reproducing a charge, somewhat analogous to that of a Leyden jar, which was discharged so soon as a conductor allowed the fluid to pass. The idea of resistance is the necessary corollary of the conception of a force doing some kind of work§, whereas the idea of conducting-power is the result of an obvious analogy when electricity is conceived as a fluid, or two fluids, allowed to pass in different quantities through different wires from pole to pole. When submitted to measurement, the

\* Phil. Trans. 1821, vol. cxi. p. 425.

† Ann. de Chim. et de Phys. vol. xxxii. 2nd series, p. 420.

‡ Die galvanische Kette, mathematisch bearbeitet, 1827; also Taylor's Scientific Memoirs, vol. ii. p. 401.

§ The writer does not mean by this that electrical and mechanical resistance are truly analogous, or that a current truly represents work.

Fig. 1.

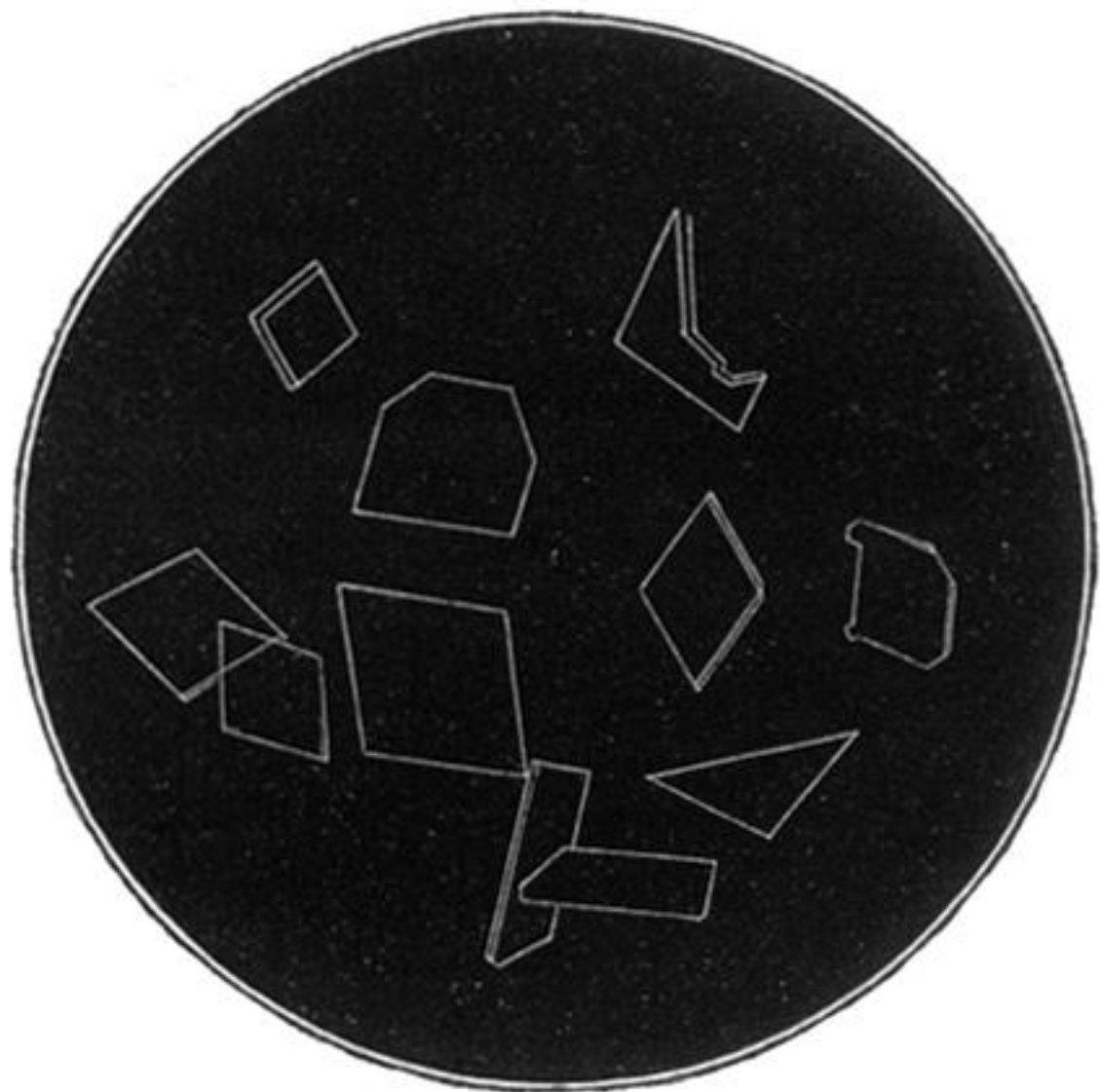


Fig. 2.

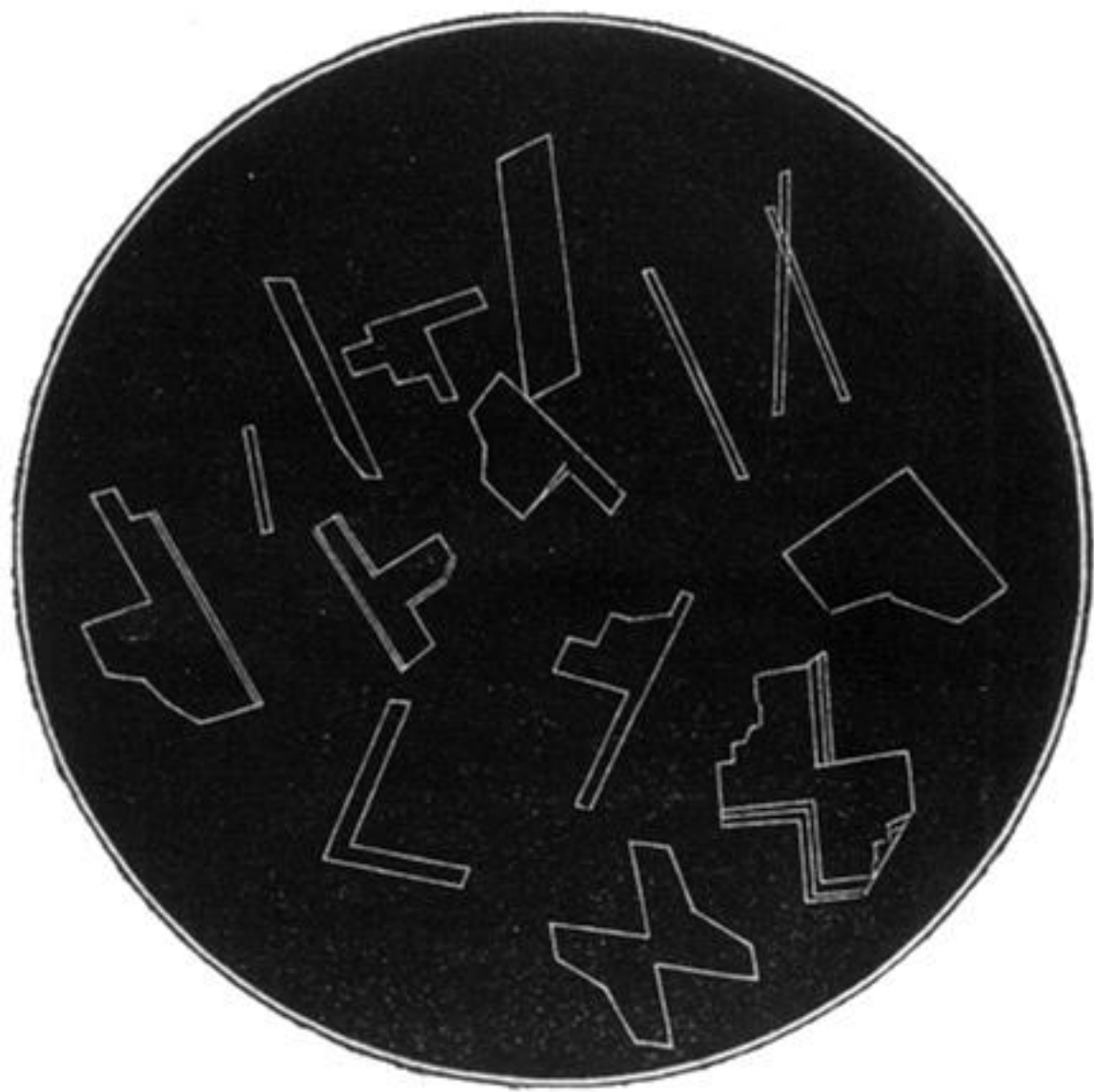


Fig. 3.

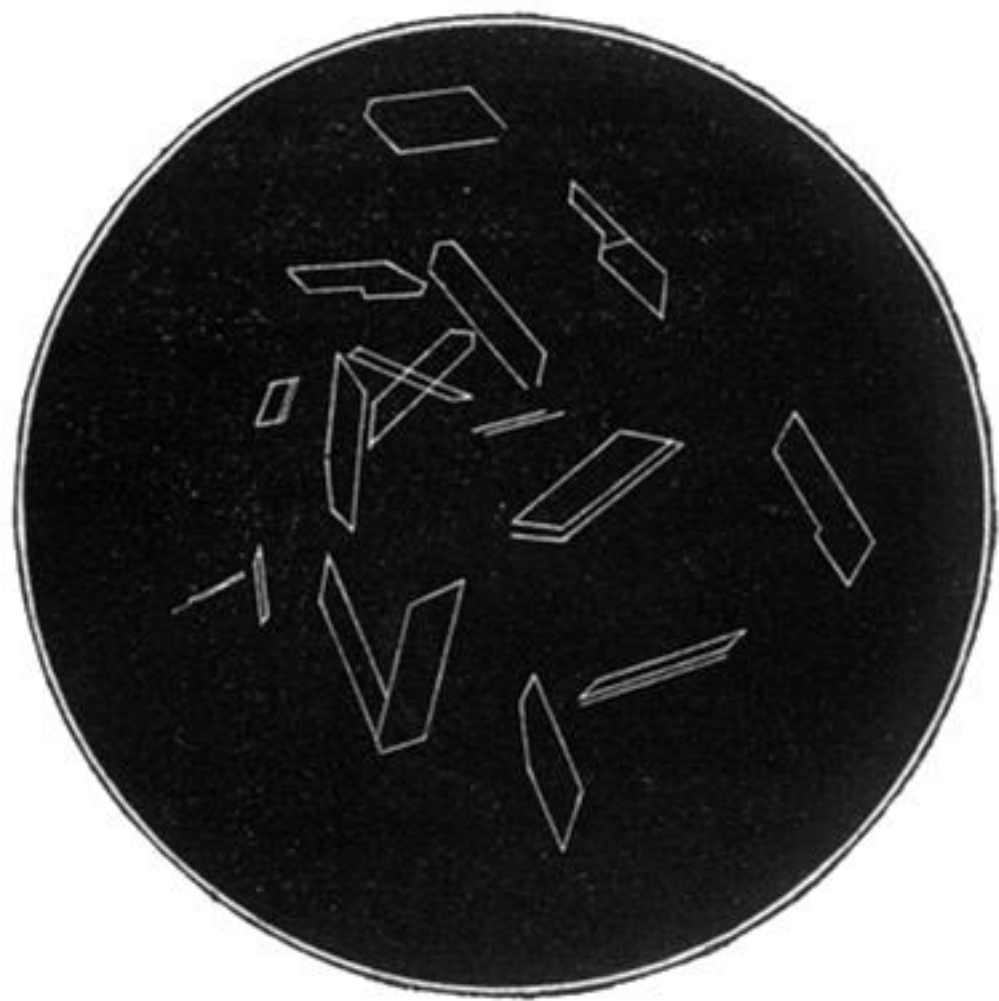


Fig. 4.

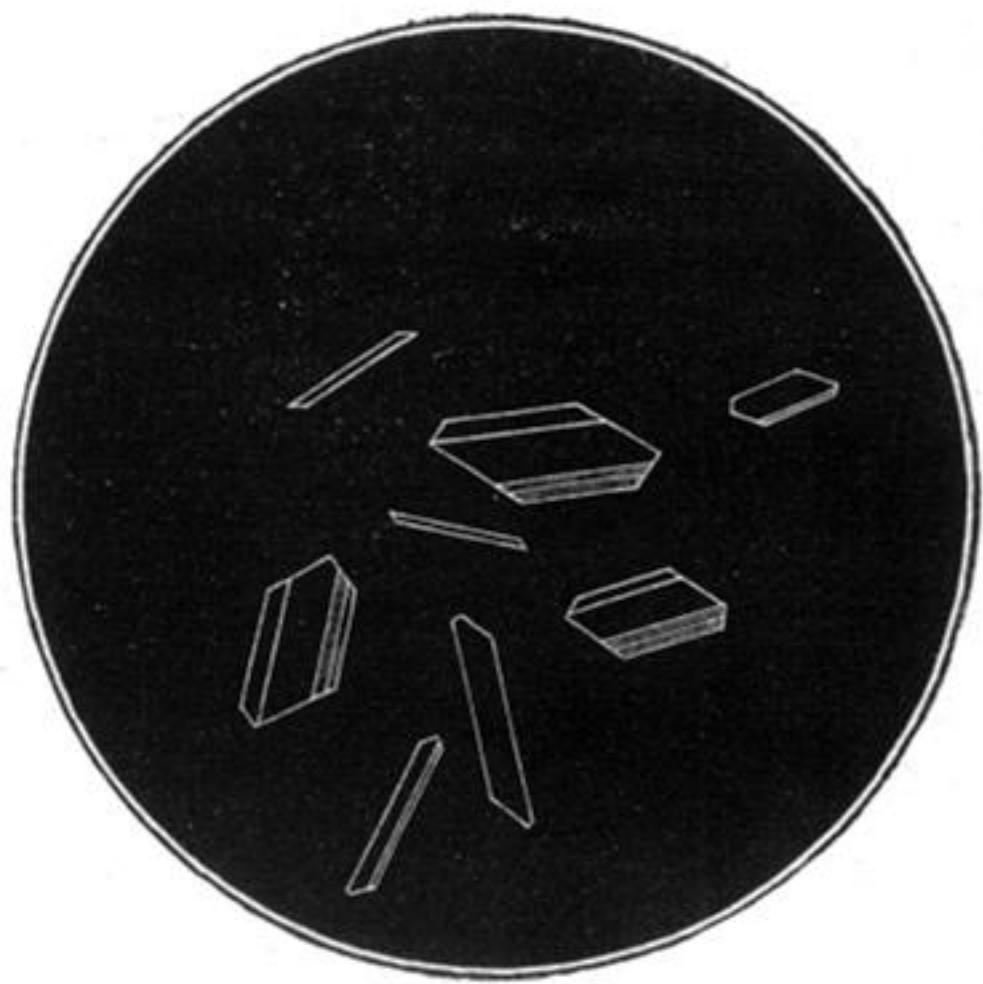


Fig. 5.

