

deposition of the metallic sulphide from its hyposulphite solution. Still, the material is the same in each case, and I doubt not but that, as deposited upon the comparatively fixed minerals, the artificially-produced film will prove to be quite as durable under ordinary atmospheric conditions as those which nature has so laboriously and sparingly deposited:

In conclusion, I would draw your attention to the artificially-prepared chromes on the table, and to the glass slides, on which, at the suggestion of Mr. McKay, I have spread a quantity of the covellite-coated galena sand, in order to show the adaptability of these chromes for ornamenting picture-frames.

ART. XLVI.—*On the Fallacy of the Electro-capillary Theory.*

By WILLIAM SKEY, Analyst to the Geological Survey.

[Read before the Wellington Philosophical Society, 3rd October, 1888.]

Two theories have been advanced by scientists to explain the action which takes place when aqueous solutions of potassium sulphide and cupric sulphate come in contact with each other in Becquerel's electro-capillary cell.

Becquerel, who originally discovered this phenomenon; and who by its means afterwards produced, or, rather, imitated, a large number of natural minerals, supposed it to be due to a combination of a physical force with that of electricity, to which he applied the term "electro-capillary action." Speaking of the deposition of the copper, he says, "The two liquids, acting on one another through the capillary space, form a galvanic couple, the circuit being completed in the first instance by certain parts of the walls of that space, and afterwards by the separate metallic particles. The correctness of this view may be shown by dipping the ends of a bent copper wire into the tube-apparatus above described, so as to form an ordinary galvanic circuit of two liquids and a metal. The end of the wire dipping into the alkaline solution is then attacked, and forms the positive pole, while that which dips into the copper solution forms the negative pole, and becomes covered with metallic copper; at the same time thiosulphate and nitrate of sodium are formed, and the copper nitrate is decomposed; but no trace of metallic copper is formed, either on the crack or on the adjacent portions of the tube. As soon, however, as the wire is removed, the crack and the inner surface of the tube become covered with metallic copper. This shows

that in the absence of the wire its conducting function is discharged by certain parts of the walls of the capillary space." He further says that the chemical action between two liquids separated by a capillary partition is determined mainly by the magnitude of the electro-motive force; and that the intensity of the electro-capillary current depends upon the chemical attraction between the liquids, and the size of the pores, the diameter of which should be such that all the electricity produced by the contact of the liquids may be utilised for the production of the current.

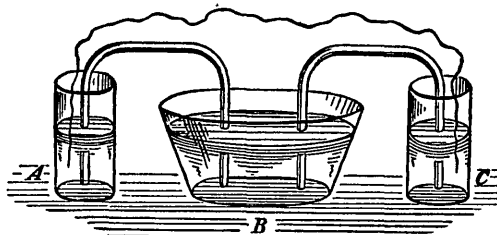
Loew objects to this hypothesis, and in the "Journal of Practical Chemistry" says he is of the opinion that all Becquerel's results may be explained without calling in the aid of electric currents, and he proposes to designate the mode of action by the name of chemosmose.

Loew supports his opinion by stating that when a crystal of cupric sulphate is immersed for some hours in a solution of potassium sulphide, there will be found under the black crust of cupric sulphide which rapidly forms on the crystal a quantity of metallic copper. He says that when a crust of cupric sulphide is once formed the process of decomposition will go on as before only when the molecular gaps (in the crust) are wide enough to allow of the passage of more molecules of potassium sulphide, whilst when the gaps are too small chemosmotic decomposition or electro-capillary action will be produced. The potassium unites with the group SO_4 , metallic copper being separated, while the sulphur previously combined with the potassium remains outside the crust, forming potassium disulphide. In reality he assumes that osmose, as favoured by capillary spaces, supplements the effects of chemical action, and under the influence of the newly-formed power potassium sulphide is decomposed into its elements.

Now, it is clearly to be seen that both these scientists set a high value upon capillary spaces or minute pores, for they certainly wish to inculcate the idea that these possess the property of greatly intensifying chemical force—a theory so much at variance with the conclusions I have arrived at that I now propose to show you that these so-termed electro-capillary deposits of Becquerel and the chemosmotic deposits of Loew are simply the product of chemical action unaided by any other force.

The affinity of the sulphur of potassium sulphide for the copper of cupric sulphate is so strong that at the moment of combination an electric current is generated sufficiently intense to deposit copper from its solution; a fact which may be easily demonstrated by a slight variation of Becquerel's apparatus, so as to exclude the possibility of capillary action being in any way connected with this phenomenon.

Solutions of potassium sulphide and cupric sulphate are connected by two siphons filled with a solution of sodic chloride, as shown in the accompanying diagram :—



A. Potassium sulphide. B. Sodic chloride. C. Cupric sulphate.

In the solution of potassium sulphide a plate of sulphurised platinum, galena, or covelline is placed, and this is connected with a platinum electrode placed in the cupric sulphate. In a short time it will be found that the platinum which has contact with the cupric salt is covered with metallic copper, and it may be observed that this effect is produced before any film or precipitate of cupric sulphide or any other compound has formed. Clearly, then, in this instance no portion of the effect is due to capillary or osmotic force.

In Becquerel's so-called electro-capillary apparatus what really takes place is this: The first action is the formation of sulphide of copper in that part of the fissure joining the two solutions which is contiguous to the potassium sulphide. This blocks the fissure at that point, cuts it off from the sulphide, and produces a measure of electric force—in fact, a current—which, being conducted by the sulphide, finds its way to the copper solution by another part of the fissure, and, manifesting itself on the opposite side of the cupric sulphide, thereon deposits copper, which under the circumstances, being protected by a crust of cupric sulphide and the walls of the fissure, does not sulphurise, but remains as copper and forms a nucleus for succeeding metallic deposits.

Through the wider parts of the fissure the liquids slowly mix, and the cupric sulphide which forms there continues the electric currents, and so carries on the electro-deposition of copper in the fissure or along the walls of the vessel containing the metallic salt. If the wider part of the fissure is under a certain width the cupric sulphide forming may completely dissolve in the sulphide solution, and so keep the space open for the electric current.

The narrow fissure is no doubt necessary for these results, which, however, can certainly be produced by electric action without being in any way aided or supplemented by capillary force.

A wide fissure allows the diffusion of the liquids to such an extent that each atom of copper as it is reduced is immediately sulphurised, and so there is no metallic decomposition manifested. The narrower fissure allows of an electrical current being set up in one direction, thus favouring metallic depositions, and this solely by limiting the chemical action to a certain line or point. On the other hand, while wide fissures do not prevent the production of electrical currents, they hinder any ocular demonstration of their presence. The liquids mix in a confused, irregular manner, whereby innumerable currents are set up, which, having no determinate direction, either neutralise each other or form only minute metallic deposits, which almost simultaneously with their formation are sulphurised to the cupric sulphide, and thus become obliterated.

I shall now pass on to a criticism of those minor statements of Becquerel's communications upon this subject which also appear to me to be erroneous.

His suggestion that the walls of these capillary fissures conduct a current of electricity before copper is deposited thereon seems to be wrong for two reasons. First, there can be no electric current produced until copper sulphide has formed in the narrow part of the fissure; and this compound, being, as I have already shown, an excellent conductor, will certainly conduct the current. Second, as glass—the material Becquerel used for his cell—is a dielectric, and the solutions electrolytes, it is manifest that the current was conducted by the saline solutions filling the fissure itself, and not by means of its walls.

His assumption that the copper which is deposited in his cell or any part of it is due to the decomposition of the cupric sulphide is very difficult of belief. It is well known that this sulphide is a very fixed compound, the affinities of its elements for each other being very strong. Neither potassium sulphide nor cupric sulphate separately have any reducing effect upon it, and it is very improbable that any product arising from their interaction would be able to effect what they separately could not do.

In his controversy with Loew regarding the deposition of copper in capillary spaces Becquerel is undoubtedly correct in affirming the existence of electric currents; also in assuming that these are used in the deposition of the copper. His error consists in the assumption that capillarity is necessary to supplement and complete the action.

In regard to Loew's own results with cupric-sulphate crystals placed in a solution of potassium sulphide, they show that even here electric force has had a large share in producing them—that his experiments, in fact, are merely a modifica-

tion of those of Becquerel. Thus, his crystals form a series of narrow fissures or spaces between them and the bottom of the vessel in which they are placed, also a further series with the crust of cupric sulphide which forms around them, and in these spaces metallic copper is deposited by the same cause as that operating in Becquerel's cell.

On repeating Loew's experiments I have always found that the copper is deposited in a solid film on the containing vessel, and in nuggets equally coherent, proving that a concentration of the metal takes place. Each separate deposit of copper, undoubtedly performs, the part of the negative pole of a galvanic battery, this polar condition being due to the fact that they are preserved from the attack of the sulphide by cupric sulphate and cupric sulphide, with which they are surrounded. Under these circumstances electric currents must be produced, and without these to concentrate and locate the deposits the copper could not be so compact and aggregated.

Chemical decomposition alone, with its constant concomitant electricity, is certainly competent to produce all the phenomena that Becquerel and Loew have discovered. There is therefore no need, in order to explain the deposition of copper in a fissured cell, to assume that either capillarity or osmose intensifies the current of electricity.

I will only add that I have all along strictly confined myself to a discussion of the theories of Becquerel and Loew as applied to explaining the deposition of metals and metallic compounds in narrow fissures or minute pores; but if my criticisms and theory are correct, the idea of electro-capillarity as a compound force present in vegetable and animal organisms will also have to be given up. Here, as in Becquerel's cell, the only use of the capillary space or fissure is to preserve for a time that which chemical or electrical forces have produced, and this simply by the mechanical limitation which it sets upon their operations in the organisms which I have named.

ART. XLVII.—*On the Occurrence of Native Lead at Collingwood, and its Association with Gold.*

By WILLIAM SKEY, Analyst to the Geological Survey.

[Read before the Wellington Philosophical Society, 3rd October, 1888.]

(Abstract.)

A NUMBER of small rounded pieces of a soft malleable substance were forwarded to the Geological Survey Department by Mr. Washbourne, as lead, covered with the carbonate, and upon