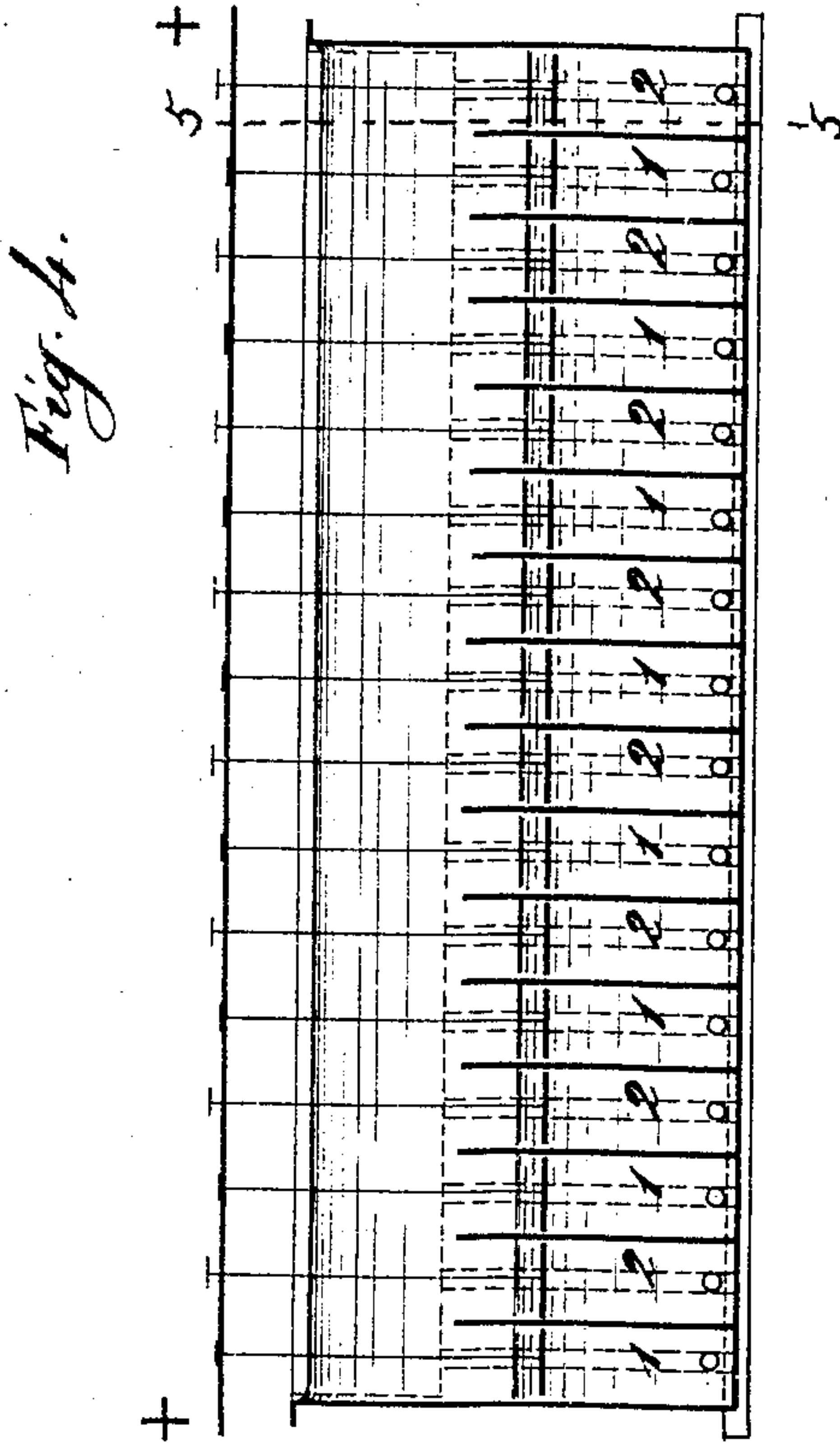
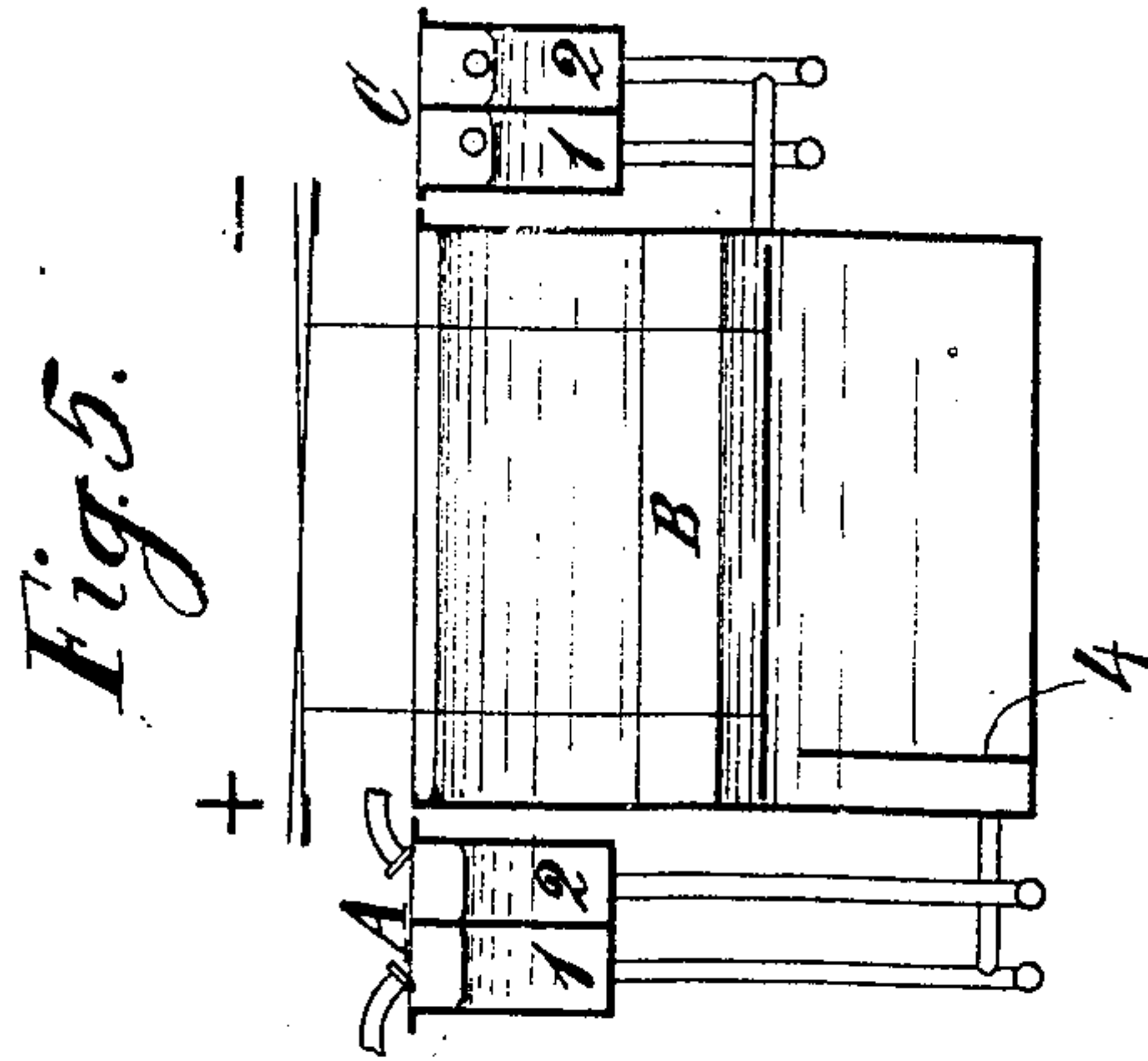
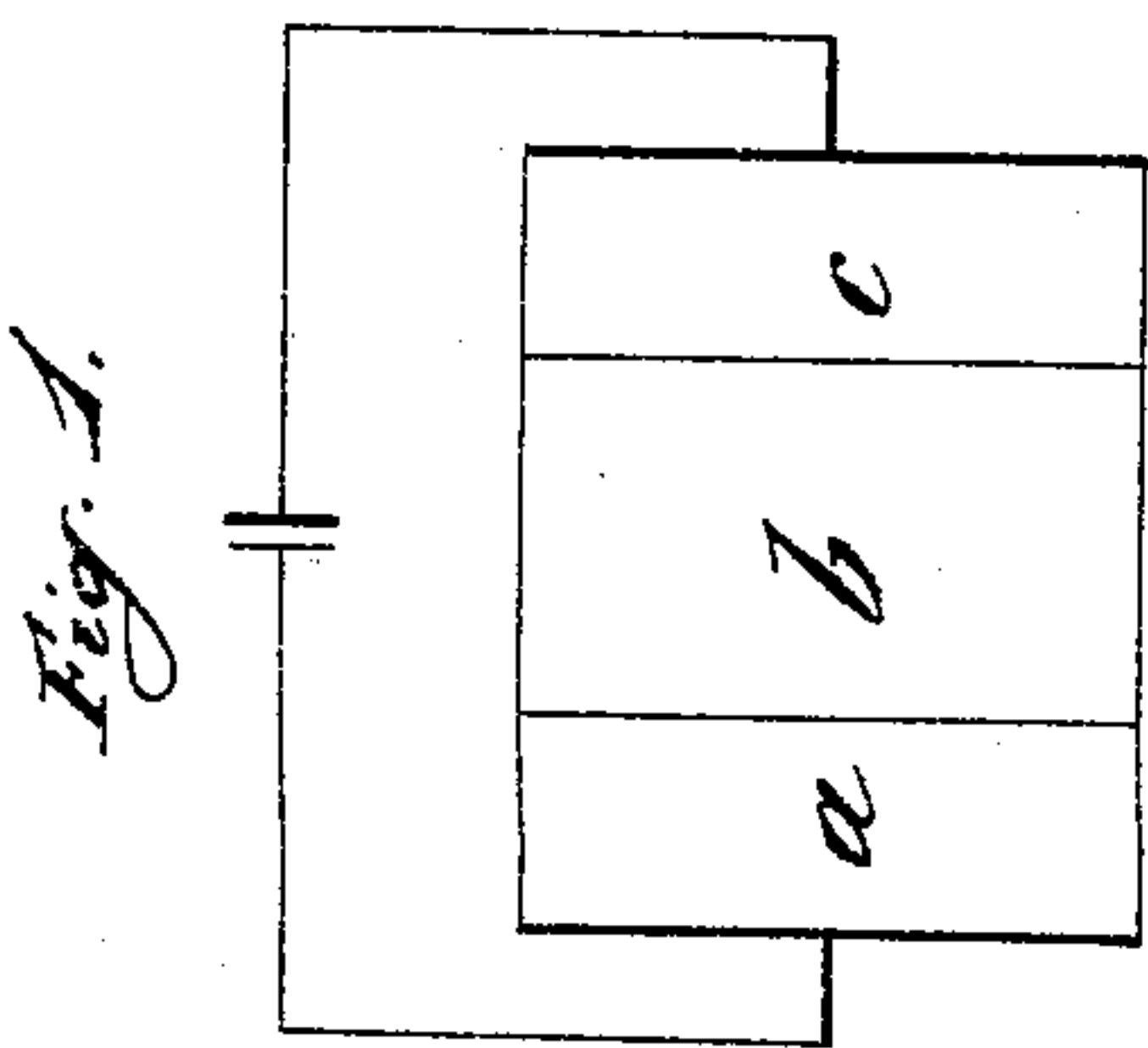
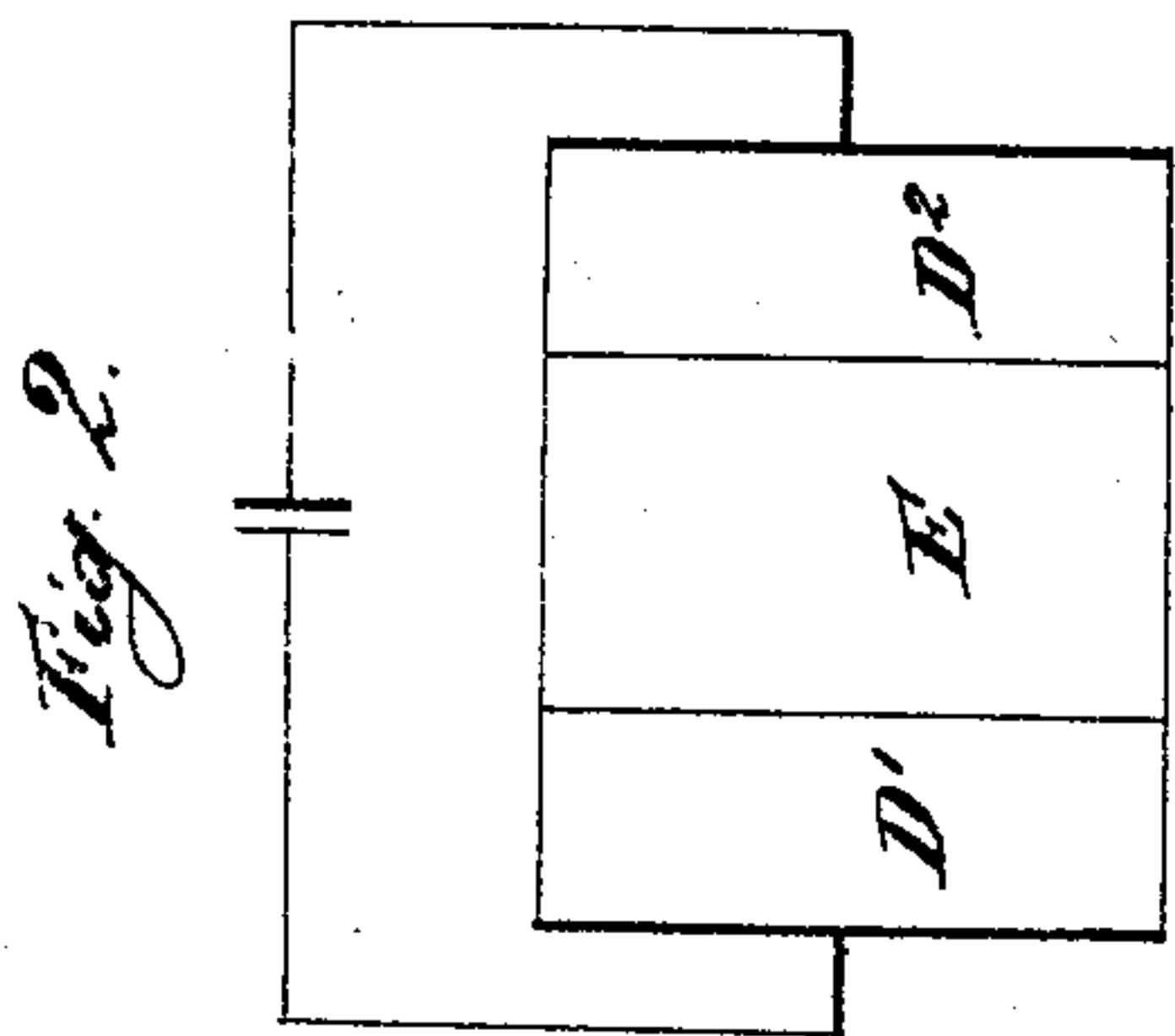
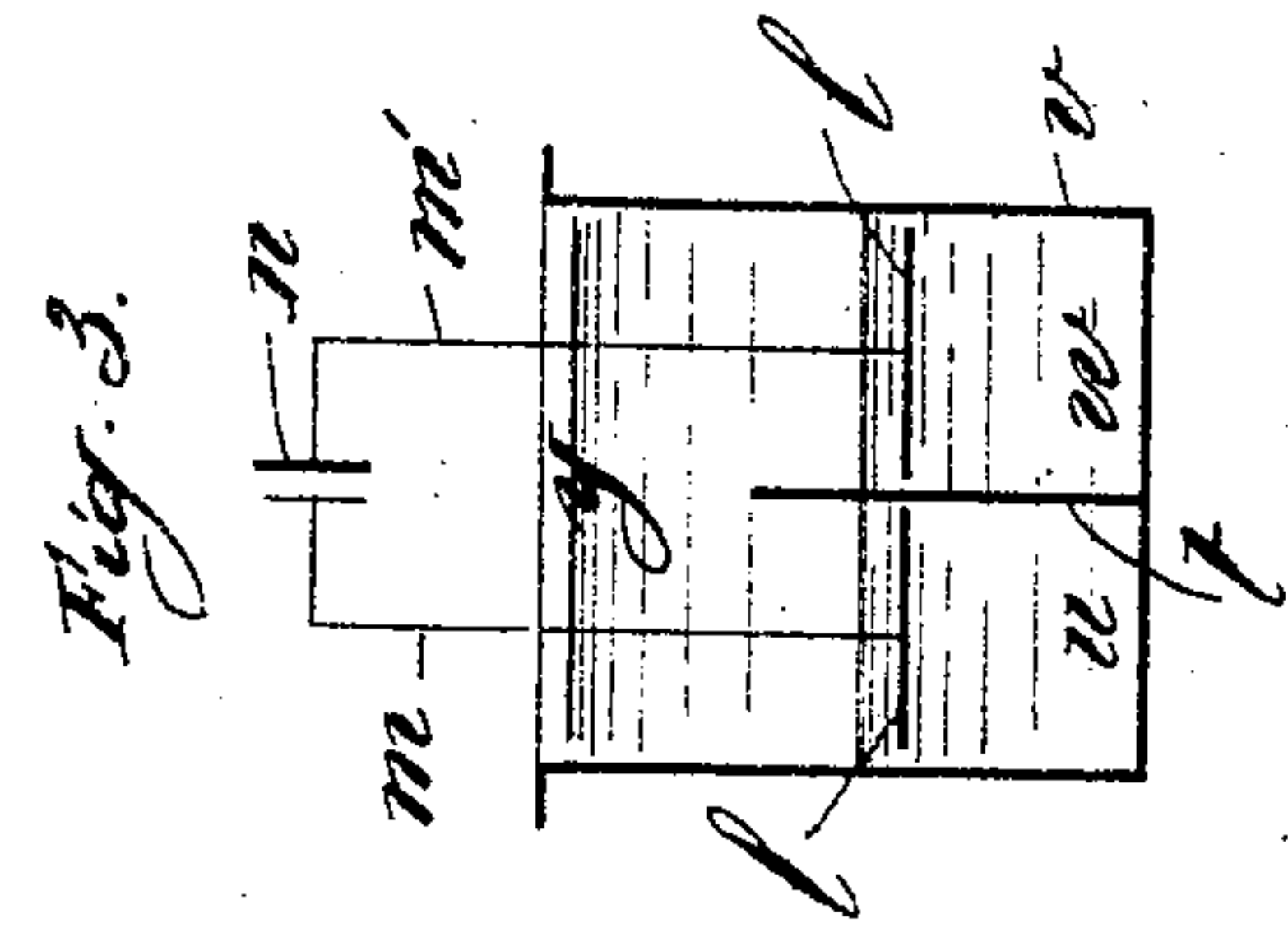


G. RAMBALDINI.

ELECTROLYSIS.

APPLICATION FILED JAN. 28, 1902.



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UNITED STATES PATENT OFFICE.

GIOVANNI RAMBALDINI, OF MINIERA DI BOCCHEGGIANO, ITALY.

ELECTROLYSIS.

SPECIFICATION forming part of Letters Patent No. 779,735, dated January 10, 1905.

Application filed January 28, 1902. Serial No. 91,599.

To all whom it may concern:

Be it known that I, GIOVANNI RAMBALDINI, mining engineer, a subject of the King of Italy, residing at Miniera di Boccheggiano, Province of Grosseto, in the Kingdom of Italy, have invented Improvements in and Relating to Electrolysis, of which the following is a specification.

It frequently happens in the electrochemical and electrometallurgical industry that it is necessary to effect electrolysis while keeping the liquids of different natures which are in contact with the two electrodes separate one from the other. This separation, as is well known, must not be complete; but while avoiding the mixture of the salts dissolved it must always permit of the conveyance of electric charges from one liquid to the other, and vice versa—that is to say, the passage of the electric current from one electrode to the other through the liquid should not be interrupted. At first the problem was solved almost always by the employment of porous partitions; but such partitions have almost invariably given bad results in practice, especially in installations of any size, owing to the number of elements. In addition to this if the electrolytic process requires that only one of the two liquids shall play a direct part in this action, while the other liquid has only a secondary action termed “depolarization,” and if it does not exert any action other than serving as a medium for conveying the ions produced by the decomposition of the first, as usually happens in cases where it is a question of separating from a mixture of different metallic salts one of these salts, the porous partition does not act and is ineffectual for the purpose for which the said separation is intended. It was therefore necessary to find a more certain and practical means adapted to entirely replace the porous partition, while at the same time obviating the grave defects of this latter, a means which would also insure the principle of independence in action of each of the two liquids in the transmission of the electric current. The problem may thus be stated in the following terms: Maintain separated two different liquids without employing membranes or diaphragms of solid

porous material, but retaining between them liberty of electrolytic transmission, in the sense of liquid electric communication for the movements or exchange of the ions, and while permitting that by the electrolytic process these two liquids may become modified and act according to two laws which, if need be, may be independent of and diverse from each other. It was natural that for replacing the porous partition, separation, owing to difference in the densities of the two liquids, should have been first of all attempted; but the mere separation of the two liquids, owing to the difference of their specific weights, even when this is possible and convenient from certain points of view, cannot fulfil the condition of preventing the immediate contact of the two liquids. The principle of difference of density had therefore to be applied in conjunction with other expedients, with the intervention of the principle of secondary actions. It is essential that the two solutions having the most suitable densities should be maintained separated by strong impermeable walls and that their electric communication should be effected, on the one hand, by the electrodes and by the ordinary metallic circuit and, on the other, by a liquid much lighter than the two solutions and situated above these latter.

Figure 1 is a diagrammatic view illustrating the invention. Fig. 2 is a similar view. Fig. 3 is a vertical cross-section through a vessel, showing its diaphragms, &c. Fig. 4 is a vertical longitudinal section through a form of apparatus embodying the invention. Fig. 5 is a vertical cross-section of the same on the line 5 5 of Fig. 4.

A circuit arranged in accordance with these principles is diagrammatically represented in Fig. 1.

Two electrodes metallically connected one with the other, the two liquids *a* and *c* being in contact with the electrodes and between them the liquid conductor *b*, which in addition to the electric charges is able to convey the corresponding ions. The intermediate liquid conductor is the “electrolyte,” properly so-called, *E*, Fig. 2. The two solutions in contact with the electrodes both serve in many instances as depolarizing agents (*D'* be-

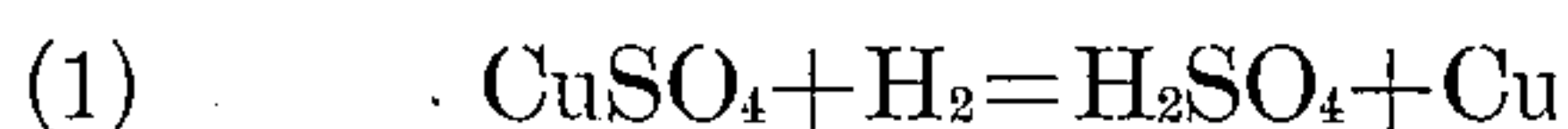
ing the positive depolarizer, and D^2 the negative depolarizer) for the two ions corresponding to the intermediate liquid, or only one if the anode is soluble. The useful work is then the effect of one or more secondary phenomena which may be produced as a result of these depolarizations. It will therefore be understood that the useful work, considered as a secondary phenomenon, may be varied in several ways by changing the depolarizing agents while keeping the third liquid invariable, especially if it is agreed to call the soluble anode the "solid depolarizer." In practice the arrangement may be that represented diagrammatically in Fig. 3. A vessel v , of non-conducting material or rendered non-conducting, is provided with a non-porous diaphragm t , also of insulating material, which terminates somewhat below the edge, which divides the vessel into two compartments u w , in which and to within a certain height from the top of the partition are the two depolarizing liquids, the positive in u and the negative in w , separated one from the other. These liquids are both covered at y by a third solution which is much lighter, and a conductor, which almost completely fills the vessel, extending much above the edge of the diaphragm. Slightly below the meniscus of separation are arranged the two electrodes l l' of any convenient form and nature, which are suspended by means of the metallic conductors m m' , which are insulated where they are immersed in the liquid and are connected externally to a source of electrical energy n . Generally speaking, it is advantageous to employ as third liquid a dilute solution of the acid which is combined with the salt which it is desired to decompose in order to obtain the metal or to separate from a mixture other salts having the same acid radical. Thus, for example, in the Siemens process for the electrolytic precipitation of copper from the mother-waters containing this metal in the state of sulfate the third liquid may be constituted by a dilute solution of sulfuric acid. In the Hoepfner process where the copper is in the state of cuprous chlorid the third liquid may be a dilute solution of hydrochloric acid. For the separation of sulfate of copper from the waters of cementation dilute sulfuric acid may be used, &c. This point of view responds well to all the conditions of the electrolytic process and is extremely useful from the industrial standpoint.

The industrial apparatus which I propose to employ for the practical application of my three-liquid method of electrolysis is diagrammatically represented in Fig. 4 in longitudinal section and in Fig. 5 in cross-section. In its most simple form it may be considered as the assemblage of three vats A B C, communicating one with the other by means of two series of lower tubes. The first series establishes communication between A and B

and the second between B and C. As shown in the drawings, the tubes proceeding from A terminate in the middle vessel B in close proximity to its bottom. Those proceeding from the vessel C enter the vessel B slightly below the surface of the lower liquid contained therein. In order to obtain the complete separation of these liquids, the two lateral vats A C are both divided into two longitudinal portions 1 2, entirely separate one from the other, while the middle vat B is divided into several transverse compartments by diaphragms 4, which, however, only extend slightly above the outlet-orifices from B to C and terminate well below the top. The tubular communications between the three vats are such that one of the longitudinal chambers of each of the vats A C (1, for example) is able to communicate with the series of uneven number of the compartments of the vat B, while the other chamber, 2, is in communication with the series of even number. For the sake of clearness and in order to show how this apparatus may be employed practically and the manner of its operation I will now describe the particular case of the separation of sulfate of copper from the waters of cementation; but of course the manner of application does not vary in other cases where the system of electrolysis above referred to is suitable, so that the considerations which follow may be readily generalized.

As is well known, the waters of cementation are a mixture of sulfate of copper with other metallic sulfates, among which are generally found in great preponderance sulfates of iron. After any suitable and readily-effected preparation which is capable of converting the ferric sulfate into ferrous sulfate these waters at the maximum density compatible with the normal temperature for their treatment are caused to fill the cells of even number of the vat B, while the cells of uneven number are filled with a solution of sulfate of copper at 20° to 25° Baumé. In both series of cells the solutions are caused to rise some centimeters higher than the right-hand upper orifices, and above these solutions water acidulated to 10° to 15° Baumé with sulfuric acid is carefully poured almost up to the edge of the vat in such a manner as to establish a sharp division between this liquid and the two lower solutions. The compartments 1 of the two small lateral vats are filled simultaneously with a solution of sulfate of copper and the vats 2 with mother-waters—that is to say, with waters of cementation. In the condition of repose the free levels will arrange themselves at such heights that all the liquid-columns reduced to the same specific weight establish equilibrium through the tubes. Beneath the menisci of division and some centimeters below it are horizontally arranged the copper or copper-covered elec-

trodes of suitable form, suspended from above by the electric conductors, which, as already stated, should be insulated where they are immersed in the liquid. These conductors are fixed to a horizontal transverse bar in any manner which will permit of metallic communication between the vertical rods and the two longitudinal conductors arranged laterally at the top of the vat B. The bars of the cells of uneven number establish metallic contact with the positive conductor; those of even number with the negative conductor only. The metallic circuit is closed upon an external source of energy, and the current on reaching the electrodes No. 1 is able to pass through the liquid to the electrodes No. 2, surmounting the partitions, and thence it is able to pass back to the metallic circuit. In this particular case the electrolytic process is effected in the following manner: The electrolyte (sulfuric acid) is decomposed into its two ions H_2SO_4 . H_2 proceeds to the negative pole, and in presence of the sulfate of copper of the waters of cementation it again forms sulfuric acid and precipitates upon the cathode metallic copper.



The sulfion SO_4 proceeds to the positive pole. It cannot become fixed upon the liquid in contact with the electrode, because the sulfate of copper is already a stable compound, and it continues to the anode, where with the metallic copper it forms sulfate of copper.



The solution of sulfate of copper at the positive pole again becomes charged with sulfate of copper, while the original solution at the negative pole gradually yields up an equal quantity of sulfate. There is therefore obtained a solution of copper on the one hand and a precipitation of the same quantity of copper on the other. The sum in absolute value of the electric charges and also their energy of position do not change in the midst of the liquid. The work of the current is therefore here reduced to overcoming the resistances of the bath. The characteristic equation of the electrolysis becomes in this case

$$(3) \quad e = ir$$

where e is the difference of potential at the electrodes, r the resistance of the bath, and i the intensity of the current. The useful work obtained is due to a secondary phenomenon, because it is the effect of the depolarization at the anode, which being soluble acts as a depolarizer, and is in this case a liquid—that is to say, the solution of sulfate of copper formed in contact with the electrode. The depolarizer—that is to say, the soluble anode—is constantly regenerated at the cathode as a new effect of depolarization. In this arrangement the efficiency is the highest possible—that is to say, theoretically, one hundred per cent. less the trifling loss due to heat—because all the sulfate of copper which is formed at the positive pole remains there and may be collected integrally, and the different velocities of the two ions SO_4 and Cu , the transfer of which constitutes the phenomenon of the electrolysis, is the reason why the losses of concentration arising from the electrolysis at the anode and at the cathode are in the same respective ratio one with the other, but inversely to these velocities—that is to say, as one to two. This consideration of the different velocity of transference of the different ions dissolved applied to the electrolysis of the third liquid has as a consequence that when an equivalent of copper precipitates at the cathode or dissolves at the anode there are wanting at the anode 0.79 equivalents of sulfuric acid approximately and at the cathode only 0.21. For this reason there remain finally in the mother-waters of cementation only 0.79 equivalent of acid instead of the entire equivalent which is regenerated there in accordance with 1. This part of acid, which can no longer be employed for the electrolysis, represents in this case a real consumption and conjointly with that which passes in the same mother-waters by the effect of the diffusion from above and with that employed also in the form of water acidulated to five to fifteen per cent. for correcting the diffusions of salts from below upward in the third liquid will constitute an expense with which the treatment must be charged. Experience, however, shows that this acid may be utilized for other operations of the hydrometallurgical process, of which electrolysis is only one of the phases. The addition of the acid, which gradually decreases in the third liquid, may be made partially in the solution of sulfate of copper during its circulation and partly directly from above, suitable precautions being taken. The electrolytic process is in this particular case of a nature to oppose an obstacle to the diffusion through the menisci of division of the liquids by fixing toward the electrodes the respective depolarizing solutions. Experience shows also that a transfer of the unelectrolyzed salts takes place and that it is shown always in the direction of the current to which it is proportional, and, finally, which depends solely upon the ratio between the quantity of unelectrolyzed salt which is considered and the sum of this quantity and of those of all the other salts dissolved, including that which is electrolyzed. This transfer of the unelectrolyzed salts, which is not prevented by the simultaneous presence of the acid of the same nature, (it is facilitated even,) acquires in this particular case, as in any other case of three-liquid electrolysis, considerable importance, because it serves to prevent at the negative

pole diffusion upward of all the salts dissolved in the corresponding solution, which the object of the electrolytic process is to separate from the salt which takes an active part in the electrolysis or which merely must not be allowed to pass into the third liquid and thence also in the other liquid to the positive pole, and vice versa.

The apparatus is capable of continuous and industrial operation.

The necessity for renewing the two lower solutions, which have already attained the greatest possible degree of modification due to the nature of the electrolytic process, is obvious, and since it is always advantageous to agitate as energetically as possible the liquids in contact with the electrodes this exchange should take place continuously and with a movement as energetic as is possible, having regard to the fact that the third liquid should not be disturbed at all, so as not to displace the menisci of separation of the liquids. Now the apparatus is constructed in such a manner as to permit of a sufficient continuous circulation of the lower liquids, while at the same time leaving the third liquid at rest.

If after having effected the charging as described with reference to the particular case above described and when all is in equilibrium a fresh solution mixed with metallic sulfate is caused to enter the vat A, this solution can pass from A into the cells of even number of B and from these into 2 of the vat C without the upper liquid taking part in the movement, and if the compartment 2 of C has been provided with a distributor and the admission to A has been suitably regulated after a few moments a condition of hydrodynamic equilibrium is obtained such that as much mixed solution enters 2 vat A as leaves 2 vat C (circulating continuously through B) without displacing there the menisci of separation of even number. This depends upon the appropriate arrangement of the tubes and upon the difference in density of the lower liquids and of the third liquid. The conditions of separation between the liquids No. 2 and the liquid No. 1 are not thereby disturbed, and this second liquid No. 1 will also remain perfectly tranquil. When once the regimen of this first circulation, which I will call "No. 2," has been established—that is to say, when once it has been arranged that there enters 2 of the vat A a given quantity of liquid and that the same quantity leaves 2 of the vat C—the circulation No. 1 may be initiated (this solution being a solution of sulfate of copper in the present case) in the same manner, and if all has been well proportioned the regimen will not vary for either of these two circulations, while the supplies at the admission and at the outlet remain the same. Consequently the menisci of division in B will always retain their absolute positions, and in

order to be the more certain that all the menisci of uneven number shall be at the same level and that those of even number may also be at the same level it is only necessary to effect communication between the vertical tubes of uneven number at their lower portion and those of the other series, respectively, because they all establish, as has been stated, communication of the vat B with the two lateral vats. These lower communications, if they are effected by means of longitudinal tubes, which may be opened at one end, will also serve for emptying the three vessels simultaneously when necessary. Finally, by means of suitable partitions arranged within the cells of B the movement of the liquids may be regulated in such a manner that it corresponds more to the object for which the circulation is intended. It is obvious that a series of these vessels may be arranged in the manner of a cascade, obtaining from all of them an operation which is absolutely reliable and constant if after having established a given regimen care be taken to maintain constant the supply of liquid entering the first apparatus of the said series. In this manner and by sufficiently increasing the number of elements it may be arranged that the liquid which enters the first leaves the latter only when it has attained such a degree of transformation that it is no longer adapted to be employed for the electrolytic process. In the particular case under consideration the mother-waters of cementation may be caused to issue exhausted or almost completely exhausted of copper, while the solution of sulfate of copper at its issue will have acquired the greatest degree of density compatible with its temperature and with the necessity of not forming crystals in contact with the electrodes. At this point such a solution is able to pass to concentration and crystallization in order to again enter the cycle of operations sufficiently diluted.

What I claim, and desire to secure by Letters Patent of the United States, is—

1. A non-conducting vessel, an insulating-partition, liquids in said vessel upon opposite sides of said partition, an electrode in each compartment in contact with the liquid therein, metallic conductors supporting said electrodes, a lighter and conducting liquid in said vessel and covering the liquid in its compartments, said partition terminating in said lighter liquid beneath the surface thereof, and a source of electrical energy externally connected with said metallic conductors.

2. A series of vats containing liquid and subdivided, a communication between the compartments of one vat and the adjacent vat near the bottom, a communication between the compartments of the other vat and the adjacent vat at a point in proximity to the upper level of the liquid therein, the intermediate

vat having a series of transverse diaphragms
terminating below the surface of the liquid
therein, the communication between the cen-
ter vat and the others being alternately dis-
5 posed with relation to the compartments of
the intermediate vat, substantially as de-
scribed.

In testimony whereof I have hereunto set
my hand, in presence of two subscribing wit-
nesses, this 10th day of January, 1902.

GIOVANNI RAMBALDINI.

Witnesses:

EMILIO MASI,

ANTONIO MARISONDI.