

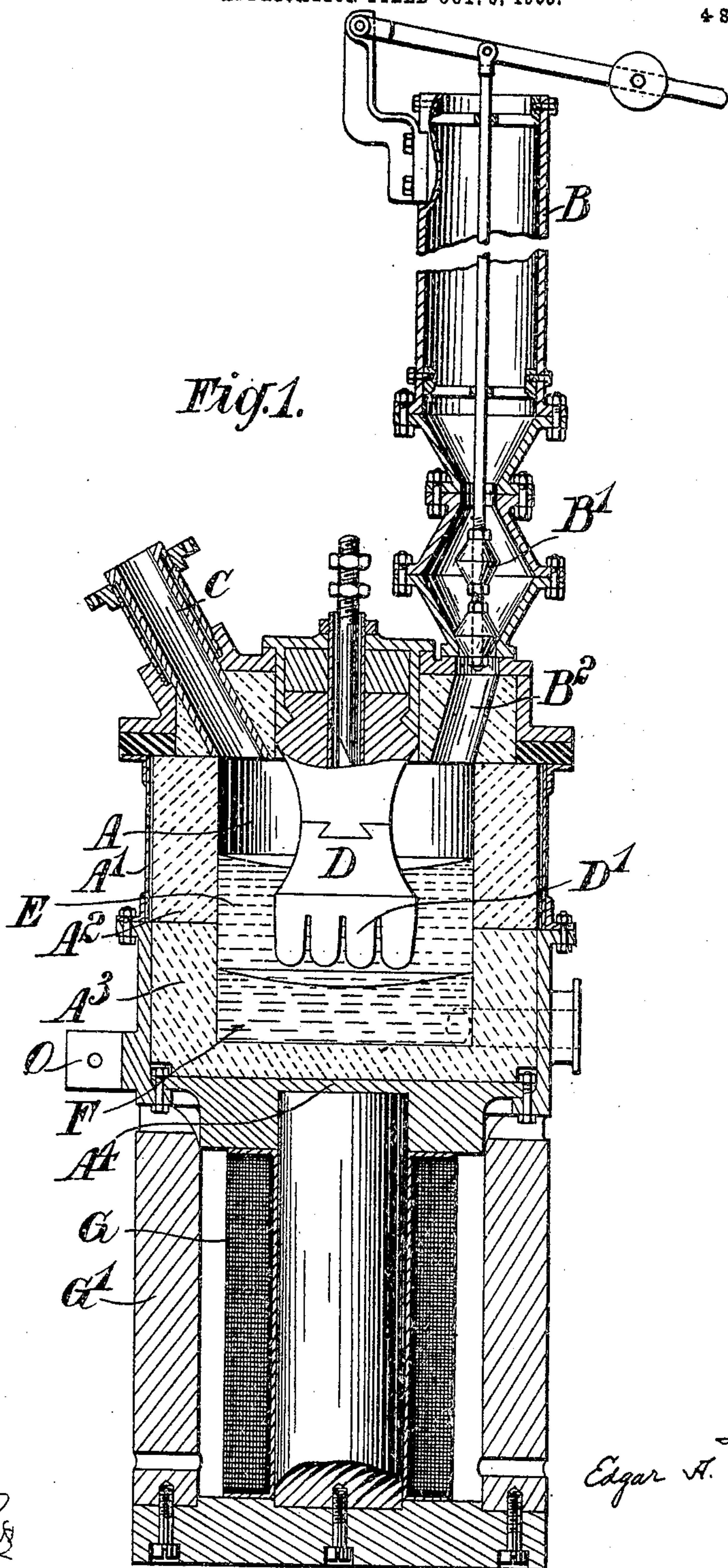
No. 801,199.

PATENTED OCT. 10, 1905.

E. A. ASHCROFT.
PROCESS FOR THE PRODUCTION OF METALS OF THE ALKALI GROUP
BY ELECTROLYSIS.

APPLICATION FILED OCT. 3, 1903.

4 SHEETS—SHEET 1.



Witnesses;
Harold H. Hays
Mabel Hayes.

Inventor:
Edgar A. Ashcroft.

By *Knights Bros*
Attorneys

No. 801,199.

E. A. ASHCROFT.

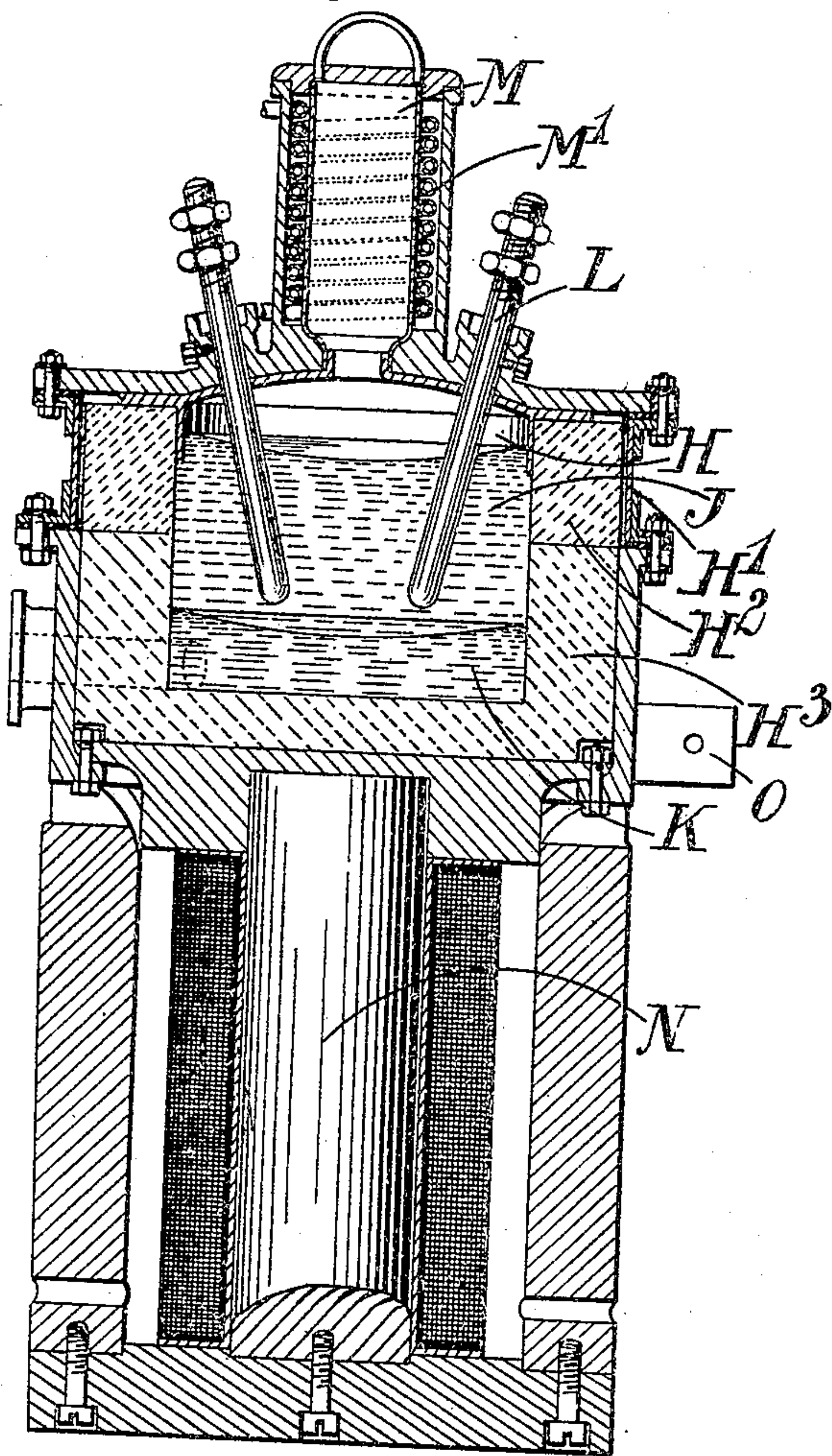
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Fig. 2.



Witnesses;
Carolsrud
Mabel Hayes

Inventor
Edgar Ashcroft
By Knights Bros
Attorneys

No. 801,199.

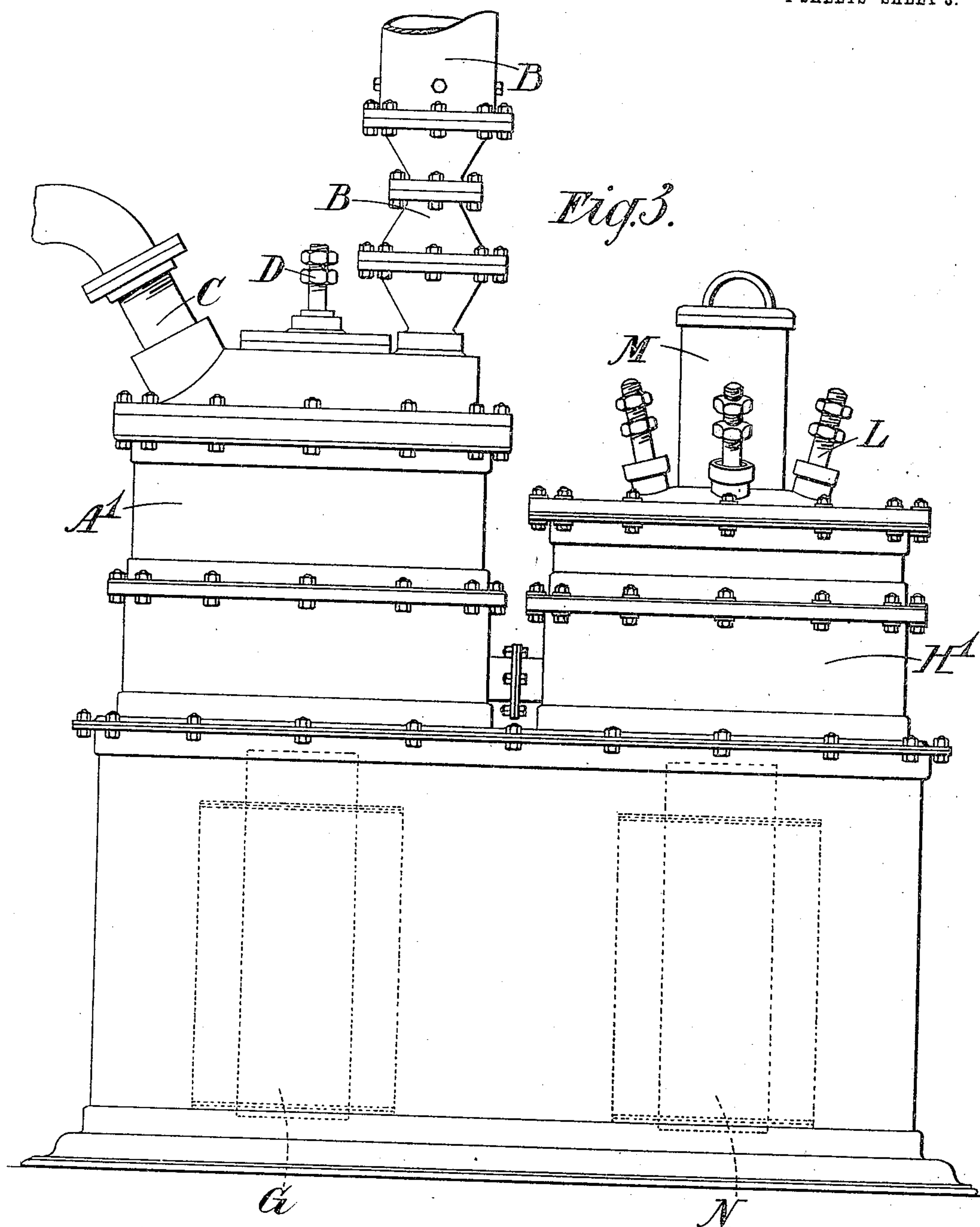
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Mabel Hayes

Inventor;
Edgar A. Ashcroft
Be Knight Bros
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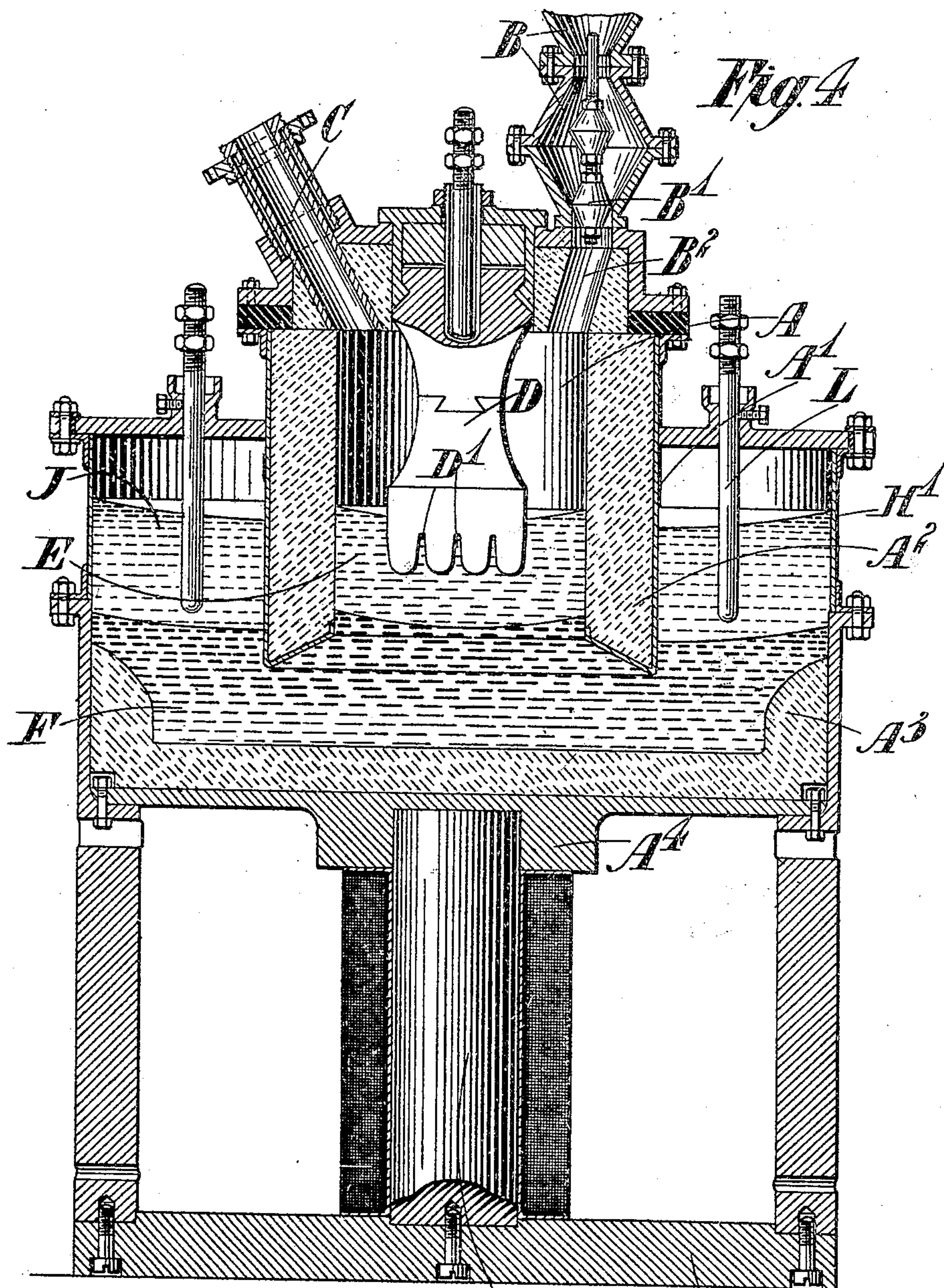
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4 SHEETS—SHEET 4.



Witnesses
Harold W. Wadsworth
Mabel Hayes

Inventor
Edgar A. Ashcroft
By Knight Bros.
Attorneys

UNITED STATES PATENT OFFICE.

EDGAR ARTHUR ASHCROFT, OF WESTON, VIA RUNCORN, ENGLAND.

PROCESS FOR THE PRODUCTION OF METALS OF THE ALKALI GROUP BY ELECTROLYSIS.

No. 801,199.

Specification of Letters Patent.

Patented Oct. 10, 1905.

Application filed October 3, 1903. Serial No. 175,715.

To all whom it may concern:

Be it known that I, EDGAR ARTHUR ASHCROFT, a subject of the King of England, residing at Weston, via Runcorn, in the county of Chester, England, have invented a certain new and useful Improved Process for the Production of Metals of the Alkali Group by Electrolysis, of which the following is a specification.

My invention relates especially to the production of metallic sodium and the like metals from the chlorids.

In carrying my improved process into effect I prefer to employ a two-compartment cell and an intermediate electrode; but the operation can also be performed in two separate cells and the sodium lead or like alloy transferred mechanically from one cell to another and the depleted carrying agent mechanically returned to the first cell for use again.

In the production of sodium the following apparatus may be employed: The first cell contains an electrolyte of fused sodium chlorid and carbon anodes or part carbon and part lead anodes depending from above. The cathode is of fused lead or other suitable metal fusing at a moderate temperature and making a fusible and mobile alloy with sodium. The temperature in the first cell is above the fusion-point of salt, therefore approximately 750° to 850° centigrade. The second cell contains, preferably, an electrolyte of sodium hydrate; but any other suitable medium may of course be used, notably sodium chlorid, bromid, iodid, or other like salts or mixture of salts, such as barium, calcium, strontium, sodium, potassium, chlorids, or iodids fusing at a low temperature. This cell may have a cathode of nickel or iron, and the anode is the fused alloy passing into it from the first cell. The contents of each cell are caused to swirl more or less violently, preferably by an electromagnetic device or by other suitable means, and a systematic transference of the intermediate electrode is caused to take place into and out of each cell through suitable passages. The action of the apparatus is then as follows: Chlorin is set free at the anode of the first cell and escapes to the surface of the electrolyte and thence out of the apparatus. Sodium is deposited at the cathode and alloys with the circulating lead, passing thus into the second cell, where it becomes an anode. At the cathode of the second cell sodium is set free, and if wet sodium hydrate is present some hydro-

gen also is produced and escapes. The sodium is readily collected and at the temperature of working, when caustic soda is employed as the intermediate electrolyte, is not readily ignited. When, however, sodium chlorid or other high-fusion medium is so employed, the sodium must be carefully guarded from the outer air until sufficiently cooled. The temperature of the second cell when employing caustic soda must be very carefully regulated, which can be accomplished by various devices, especially to avoid overheating by the incoming alloy from the hotter cell. The temperature in the second cell is somewhat above the fusing-point of caustic soda, therefore approximately 300° to 350° centigrade when sodium hydrate is employed. With sodium iodid the temperature of the second cell is about 650° centigrade, just above the fusing-point of this salt, and when sodium chlorid is the medium the two cells may have the same temperature. In carrying out my invention I have used a current density in the second cell of my apparatus of from two to ten amperes per square inch of anode-surface and approximately ten amperes per square inch of cathode-surface. The current density in the first cell may be according to known practice, which varies considerably. No oxygen or other ion escapes at the anode and no consumption of the electrolyte takes place in the second cell. Under these conditions very favorable conditions of working are established. To the first cell chlorid of sodium is regularly supplied to take the place of that decomposed.

The heating in both cells is preferably performed internally by means of the current and adjusted by varying the distance between the electrodes or the rate of current-flow. A refractory lining is required for the first cell and for the second cell when a high-fusion medium is employed. Nickel may be used for the lower portion of the two cells containing the sodium-lead alloy and is preferably backed by some heat-insulating material. An ordinary steel or metal pot is sufficient for the second cell when caustic soda is the intermediate electrolyte.

In the accompanying drawings, which represent apparatus suitable for carrying out this invention, Figure 1 is a sectional elevation of an electrolytic decomposing-vat. Fig. 2 is a sectional elevation of a secondary electrolytic vat. Fig. 3 is an outside elevation showing the two vats connected together. Fig. 4 is a sec-

tional elevation of an alternative form of electrolytic apparatus in which two cells are combined.

Like letters indicate like parts throughout the drawings.

Referring to Fig. 1, the electrolytic vat A comprises an outer shell A', of iron, lined at its upper part with fire-clay or the like A² and at its lower part with carbon A³ and a thin facing of nickel or iron. The salt-feeding device consists of a hopper B, having a valve B' discharging into the vat A through an inlet B². An outlet C is provided for gaseous products of decomposition, generally chlorine.

The anode D is one or more blocks of carbon grooved, as at D', to increase the surface and to facilitate the escape of gas produced on its surface. The electrolyte E is fused sodium chlorid, to which may be added such substances as barium, strontium, or potassium chlorid to reduce the fusing-point, neither of these named salts being decomposed in the presence of excess sodium chlorid, and the cathode F is of fused lead or other suitable metal or alloy fusing at a moderate temperature and making a fusible and mobile alloy with sodium. In order to cause the contents of the cell to swirl more or less violently, an electromagnet G is placed beneath the cell and is preferably contained in an iron pot G', which acts as a return-conductor for the lines of magnetic force. To allow the lines of magnetic force to pass into the vat, the base A⁴ is of non-magnetic metal, such as copper. Suitable electric connections are arranged to the anode and cathode.

The action of the apparatus is as follows: Chlorine is set free at the anode D and escapes to the surface of the electrolyte E and thence out of the apparatus through outlet C. Sodium is deposited at the cathode F and alloys with the lead which is systematically removed from the cell by the agency of the electromagnet G or by tapping off into a reservoir.

Referring to Fig. 2, the second cell H comprises a vessel H', of iron, lined at its upper part with fire-clay or the like H², except when caustic soda is used, when iron or steel is suitable, and at its lower part with carbon H³, faced, as before, with thin metal. The cell contains an electrolyte J of sodium hydrate or other suitable salt of sodium. The anode K consists of a bed of fused alloy of sodium with lead or the like, and the cathode comprises one or more bars L of nickel, iron, or other convenient conductor. At the top of the vessel is a chamber M for the reception of metallic sodium, and water or steam circulation-pipes M' may be employed to cool the chamber in which the sodium is collected. An agitating electromagnet N is provided as in the case of the first cell and reservoirs for filling and emptying when the cells are worked separately.

The action of the second cell is as follows:

At the cathode L sodium is set free and if wet sodium hydrate is present some hydrogen also is produced and escapes; but normally no hydrogen is produced and the full yield of sodium is obtained with the exception of trifling losses either from this electrolyte or from any other salt of sodium, notably the double iodids of sodium and potassium which fuse at a very low temperature. The sodium is readily collected in the chamber M and at the temperature of working when caustic soda is employed, as the electrolyte is not readily ignited. When, however, sodium chlorid or other high-fusion electrolyte is employed in the second vessel, the sodium must be carefully guarded from the outer air until it is cooled sufficiently.

When separate cells are employed, storage vessels must be provided for the alloy and for the depleted carrying agent and means of transferring the same mechanically.

Referring to Fig. 3, the two cells A and H may conveniently be placed together, so that the intermediate electrode may be automatically transferred from one cell to the other by means of the electromagnets G N. Tapping off and refilling are then unnecessary.

Referring to Fig. 4, the two cells may be again combined in one apparatus. In this case the decomposing-cell A is placed in the center of the apparatus and is provided with the same electrodes D F and electrolyte E, as before, the salt-feed B B' B² and chlorine-outlet C being similar to those employed in the separate cell. The shell A' and its lining A² terminate a short distance above the bottom of the vessel A³ to allow the sodium-lead alloy F to pass out to the second cell H, which surrounds the first cell. The second cell H is annular in form and surrounds the center cell, thus forming an admirable heat-conserving device. The anode is formed by the sodium-lead alloy F passing out from the first cell. The electrolyte J is of caustic soda or the like, and metal cathodes L are employed. In this case one electromagnet G serves to agitate the contents of both cells. As in most cells using an intermediate electrode the current efficiency of one cell will not be exactly that of the other owing to recombination of the products and various causes, any difference may be compensated by shunting a small part of the current past the cell which has the greatest current efficiency or by periodically short-circuiting that cell in such proportions as to keep the alloy of the intermediate electrode constant at the most suitable composition—*e. g.*, two per cent. to five per cent. A short-circuiting connection O, Figs. 1 and 2, is provided for this purpose. In like manner as a convenient means of starting the apparatus the second cell may be short-circuited until the intermediate metal electrode has taken up its normal amount of sodium, when the short circuit may be taken off and the separation of sodium commenced.

It will be manifest that many modifications of detail and apparatus may be employed without departing from the principle of this invention.

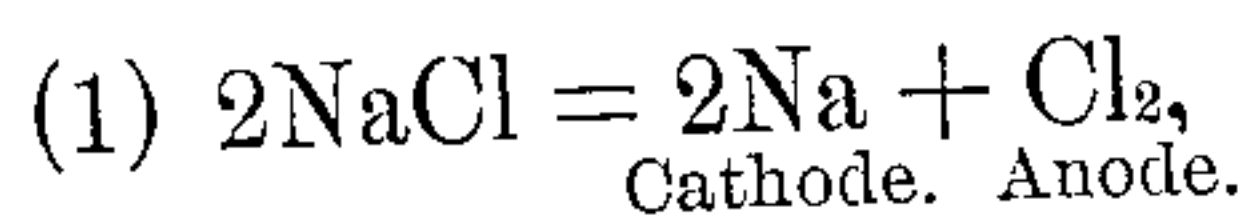
I am aware that a double cell and an intermediate electrode consisting of a metal body, (particularly mercury,) either stationary as a carrier of ions or mechanically moved by various devices, have long been employed in the manufacture of soda, &c., and that alloys of sodium and lead have been employed for the same object when electrolyzing fused salts and depleted by means of steam, air, or distillation, &c. I am also aware that electrolytic processes using fused electrolytes have been employed in which the bath is maintained fused wholly or in part by means of the current.

The employment of solutions of salt and the use of intermediate electrodes of mercury, however, are open to grave commercial drawbacks, owing to the expensive first cost, the losses of mercury, and the cumbrous and expensive apparatus which is necessary for all solution-work, which must be conducted at comparatively low-current densities and with complicated circulation of solutions and with expensive anodes.

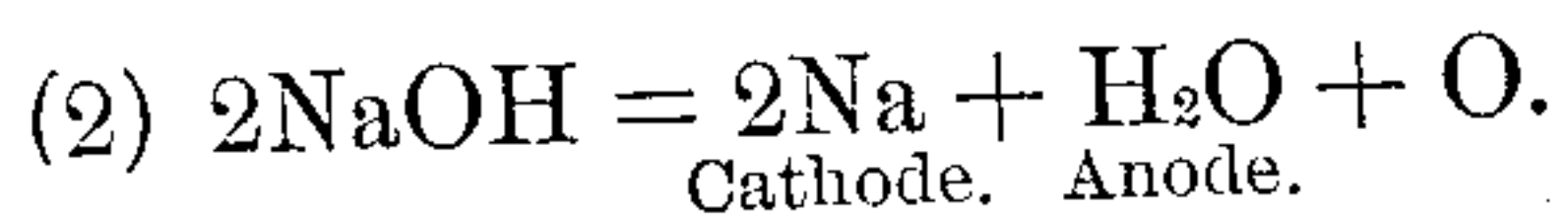
The production of sodium-lead alloys from fused salt commercially has been accompanied by serious difficulties, chief among which has been the problem of stirring or violently agitating the metal and the electrolytes, which is necessary to success.

In the removal of sodium from its alloys with lead and the like great difficulties have been experienced, and by all hitherto-suggested methods the operation is costly and troublesome. As far as I am aware it has never been previously suggested to use the alloy as an anode in a bath which is not consumed producing metallic sodium, whereby with the expenditure of very little energy I produce a practical and commercial result in an apparatus which is very permanent and compact.

In the electrolysis of sodium chlorid according to my above-described process the following reactions take place. First cell:



and in the electrolysis of dry caustic soda with the sodium alloy as anode the reaction in second cell is:



The water and oxygen then combine with more sodium from the sodium-lead alloy, and the electrolyte is therefore not consumed.

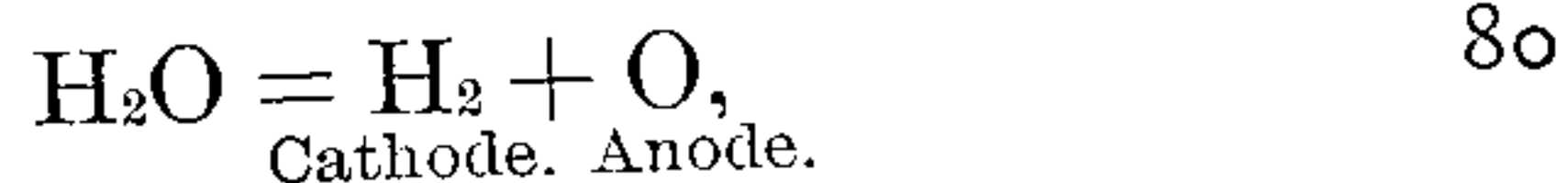
If sodium iodid or chlorid are employed in the second cell, the reaction is as follows:



in which case the sodium iodid is again reproduced.

The first cell in small units can be worked with eight volts and large units five to six, and the second cell requires less than two volts when producing sodium. The current efficiency in both cells is high under properly-regulated conditions—*e. g.*, eighty per cent. to one hundred per cent.

In the usual known manner of electrolyzing fused caustic soda with insoluble anodes the water set free at the anode recombines with the caustic, and a secondary reaction takes place as follows:



so that the operation is continuously accompanied by liberation of hydrogen, which produces explosions and also consumes much electrical energy wastefully.

In the above-described process the liberation of the sodium is accomplished quite tranquilly and the full theoretical equivalent for the current passing less slight losses is obtained.

Thus compared with the present known methods of producing alkali metals wherein a solution of caustic alkali is first produced by electrolysis and evaporated to dryness and then electrolyzed with insoluble anodes, the economy of electrical energy, as well as of other operations in the above-described process, is very great.

What I claim as my invention, and desire to secure by Letters Patent, is—

1. The process of obtaining an alkali metal which consists in providing a suitable compound of the alkali metal as an electrolyte, using an alloy of the alkali metal as an anode therein, and directly producing the alkali metal by dissolving it from said anode by a suitable current and depositing the alkali metal at the cathode without consuming the electrolyte.

2. The process of obtaining an alkali metal which consists in electrolyzing a preliminary electrolyte consisting of fused chlorid over a cathode which forms a fusible alloy with the alkali metal, thereafter providing a suitable compound of the alkali metal as a secondary electrolyte, using the alloy of the alkali metal as an anode therein, and directly producing the alkali metal by dissolving it from said anode with a suitable current and depositing the alkali metal at the cathode without consuming the secondary electrolyte.

3. The process of obtaining an alkali metal which consists in providing a suitable compound of the alkali metal as an electrolyte, using a fused alkali lead-alloy as an anode therein, and directly producing the alkali metal by dissolving it from said anode with a suitable current and depositing the alkali metal at the cathode without consuming the said electrolyte.

4. The process of obtaining an alkali metal which consists in providing a fused sodium-hydrate electrolyte, using an alloy of sodium lead as an anode therein, and directly producing the alkali metal by dissolving it from said anode by a suitable current and depositing the alkali metal at the cathode without consuming the said electrolyte.

5. The herein-described process of producing sodium which consists in electrolyzing a preliminary electrolyte consisting of fused sodium chlorid over a cathode of fused lead, and thereafter using the fused sodium-lead alloy thus produced as an anode, providing a

fused sodium-hydrate electrolyte for said alloy of sodium lead, and directly producing sodium by dissolving it from said anode by a suitable current and depositing the sodium at the cathode without consuming the secondary electrolyte. 15

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses. 20

EDGAR ARTHUR ASHCROFT.

Witnesses:

WILLIAM H. BALLANTYNE,
CLAUDE S. R. MCKENZIE.