XLI.—*The Rapid Electroanalytical Deposition and Separation of Metals. Part I. The Metals of the Silver and Copper Groups and Zinc.*

By Henry Julius Salomon Sand.

The fact that the rate of electrolytic metal deposition can be greatly increased by rapid circulation of the electrolyte has been made use of in the employment of certain processes for many years. It appears that as early as 1886 a patent was taken out by Elmore for a method of depositing copper in which the electrolytic liquid was rapidly circulated, and several other processes based on the same principle have since been introduced.*

The effect of stirring the electrolyte during the simultaneous liberation of two constituents was demonstrated by the author in 1901 in a paper on the determination of concentrations in the layer of liquid touching the electrode. It was shown in the case of an acid solution of copper sulphate that convection currents play as great a part in the determination of the ratio of the two constituents liberated at the cathode as any of the other conditions of the experiment, and in one case in which less than 40 per cent. of the current was employed in depositing copper and more than 60 per cent. in generating hydrogen, the latter effect was suppressed altogether by simply stirring the electrolyte without altering the current (*Phil. Mag.*, 1901, [vi], **1**, 45). It thus follows that the current-intensity which may be usefully employed in electrolytic metal deposition, and with it the duration of an experiment, depend entirely on the degree of stirring.

In 1903, vigorous stirring of the electrolyte for electroanalytical purposes was introduced in America almost simultaneously by Gooch and Medway (*Amer. J. Sci.*, 1903, [iv], **17**, 320, and **18**, 56) and Exner (*J. Amer. Chem. Soc.*, 1903, **25**, 896). The former rapidly rotated the cathode consisting of a platinum crucible, the latter, the anode formed of a wire spiral. The results were strikingly good in spite of the somewhat primitive methods of stirring employed, Exner in particular succeeded in reducing the time for a copper deposition to five minutes. Other forms of apparatus for rapid electroanalysis have been described by F. Mollwo Perkin (*Chem. News*, 1903, **88**, 102) and Smith and Kollock (*J. Amer. Chem. Soc.*, 1905, **27**, 1255); and of those who have published results on rapid electrodeposition, Amberg (*Zeitsch. Elektrochem.*, 1904, **10**, 383), Fischer and Boddaert (*ibid.*, 945), Smith and Kollock (*loc. cit.*), Davison (*J. Amer. Chem. Soc.*, 1905, **27**, 1275), Flora (*Amer. J. Sci.*, 1905, [iv], **20**, 268), R. O. Smith (*J. Amer. Chem. Soc.*, 1905, **27**, 1287), Price and Judge (*Chem. News*, 1906, **94**, 18) may be mentioned.

All the methods used hitherto are, however, unsuitable for the purpose for which from its very nature electrolysis with rapid stirring specially lends itself, namely, for the separation of metals by graded potential.

Although this mode of analysis was first suggested by Kiliani in 1883 (*Berg u. Hüttenmännische Zeitung*), and more fully elaborated and theoretically justified by Freudenberg working in Ostwald's laboratory in 1893 (*Zeitsch. physikal. Chem.*, 1893, **12**, 97), yet so far as

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* For an account of methods of this kind, see Sherard Cowper-Coles, *Trans. Faraday Soc.*, 1905, **1**, 218.

I am aware it has not become known to analysts to any appreciable extent. As carried out by Freudenberg, the method of separating one metal from another consisted in regulating the voltage between the electrodes so that it should always remain below the value at which the second metal begins to deposit. The maximum electromotive force which thus becomes available at any time for impelling the current through the electrolyte is equal to the difference between the deposition potentials of the two metals in question, and generally amounts to a fraction of a volt. In order that fairly considerable currents such as must be employed for rapid electroanalysis may be used, it becomes a matter of paramount importance that the electrodes should be arranged so that the resistance offered by the liquid between them is as small as possible. In Exner's experiments the pressures between the electrodes attain to 19 volts, so that his apparatus is useless for the purpose in question, and the same must be said of the other methods hitherto described.

Freudenberg's separations depend on the assumption that the polarisation of the anode has a constant value, and this restricts them considerably. A much wider range will accrue to any method which allows the potential of the cathode alone to be conveniently measured by means of an auxiliary electrode. Such a method will also become practically independent of the resistance of the liquid, and will allow separations based on a very small difference of potential to be carried out.

Having had the opportunity of designing a set of electrodes for analysis, I therefore turned my attention especially to the following points of importance.

(1) Maximum stirring efficiency, which must be fairly independent of the quantity of liquid employed, so that it may be unnecessary to evaporate the latter after each washing.

(2) Very small resistance of the liquid, to be attained by bringing the electrodes as close together as possible.

(3) The possibility of conveniently using an auxiliary electrode to measure the potential of one of the electrodes.

(4) The possibility of washing the electrodes with a minimum amount of water.

*Apparatus.**—Figs. 1*a*, 1*b*, and 1*c* illustrate the apparatus designed to meet these requirements. It consists of a pair of platinum gauze electrodes, an inner rotating electrode, 1*c*, and an outer electrode, 1*a*, which surrounds it on all sides except the bottom. The two are kept in position relatively to each other by means of the glass tube 1*b*, which is slipped through the collar *A* and the ring *B* of the outer electrode. It is gripped firmly by the former, but passes loosely

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* The platinum apparatus was made by Messrs. Johnson and Matthey.

through the latter. The hollow platinum-iridium stem *A* of the inner electrode is passed through the glass tube, in which it rotates freely. The inner electrode is designed to produce a maximum amount of rotation of the liquid, and for this purpose has a vertical partition, *P*. It is open at the bottom and as open at the top as the requirement of rigidity in the construction of the frame will allow. The mesh of the gauze is 14^2 per sq. cm. The gauze of the outer electrode almost completely stops the rotation of the liquid. While the electrolyte is therefore ejected rapidly from the centre of the inner electrode by centrifugal force, it is continually replaced by liquid drawn in from the top and the bottom. So great is the suction thus produced that when the electrode is moving rapidly, chips of wood or paper placed on the surface are drawn down to the top of the outer electrode. The circulation is practically independent of the size of the beaker employed. As the outer electrode surrounds the inner completely, the lines of flow of the current are contained between the two, and even when strong currents are employed the potential of the electrolyte any-

Fig. 1*a*.

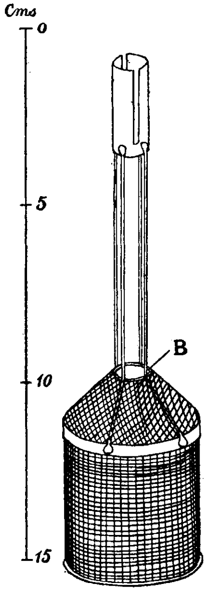

Fig. 1*b*.

Fig. 1*c*.

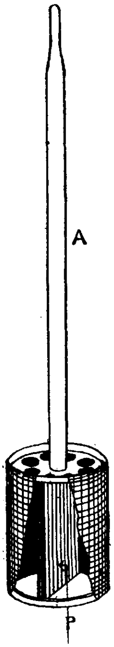

Fig. 1*a*.—Outer electrode. Fig. 1*b*.—Glass tube. Fig. 1*c*.—Inner electrode with part of gauze removed.

where outside the outer electrode is practically the same as that of the layer of liquid in immediate contact with it. This is a matter of great importance when an auxiliary electrode is employed, as it enables the potential difference electrode–electrolyte to be measured at any point in the liquid outside the outer electrode. The space between the surfaces of the two electrodes is about 3 mm. The weight of the outer electrode is about 40 grams, that of the inner electrode about 28 grams. Fig. 4 shows the stand. It will be seen that the beaker containing the electrolyte is always placed on a tripod support.

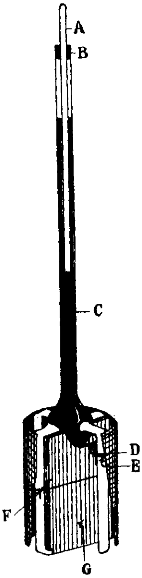

Fig. 2.—Inner electrode with glass frame. *A*, copper wire held in position in glass stem by slightly burnt rubber tube, *B*. *C*, mercury. *D*, piece of gauze fused through the glass, and, *E*, wire forming connexion between *C* and outer gauze. *G*, partition cut from microscope slide held in position by wire *F*.

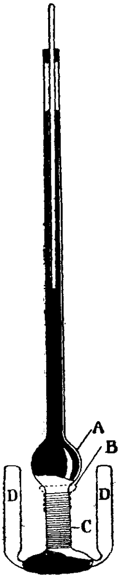

Fig. 3.—Inner electrode, No. 2. Stem and mercury as in Fig. 2. *A*, bulb to spread out gas bubbles. *B*, gauze fused into glass to make connexion. *C*, wire forming metal surface of electrode. *D*, *D*, vanes for stirring.

The outer electrode is gripped by a V-clamp, the cork from the flat side of which has been removed and replaced by platinum foil so as to obtain metallic contact. The inner electrode is held by a small chuck which is flexibly attached to the pulley from which the motion is derived. The figure will fully explain this, as well as the mode of electrical connexion by means of the mercury contained in the glass and rubber tubes *C* and *F*. There is thus practically no resistance in the rotating contact, and no chance of its being affected by the air of a chemical laboratory, a matter especially important when the potential difference of the two electrodes is measured for the purpose of separations. All movable connexions are made on the base of the stand on two sets of double terminals which are permanently joined to the holders of the electrodes by heavy flexible wire. Those parts of the stand which are exposed to the vapours from the electrolyte are painted with several coatings of a solution of celluloid in amyl acetate. In order to reduce the amount of platinum required for the apparatus, attempts were made to construct the frame of the inner electrode of

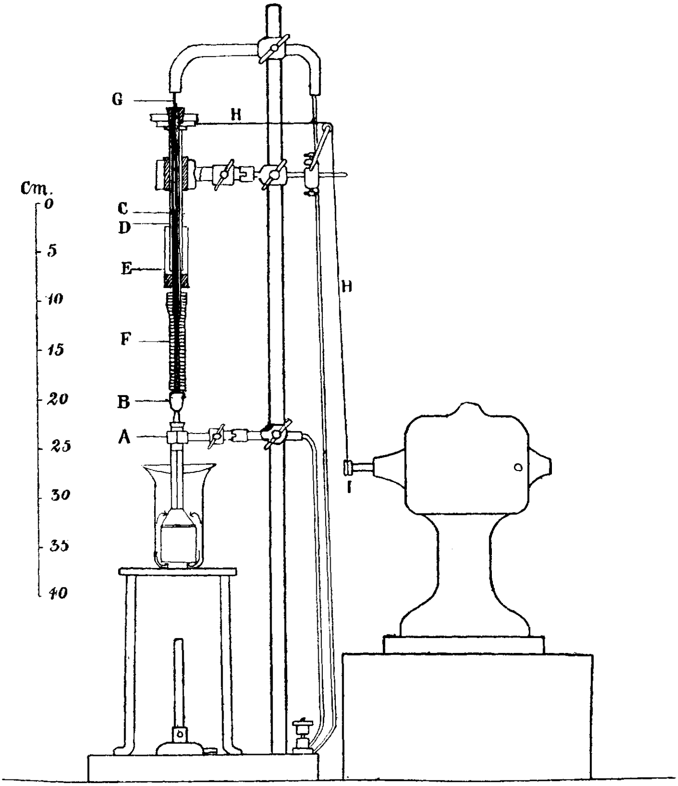

FIG. 4.—*A*, Clamp to grip outer electrode. *B*, Chuck to grip inner electrode. *C*, Glass tube rotating in glass tube *D*. *E*, Oil trap on *C*. *F*, Thick rubber tube. *G*, Amalgamated copper wire dipping into mercury contained in *C* and *F*. *H*, Cord made of violin string. *I*, Pulley made of rubber tube.

glass and at the same time to retain its essential features. Fig. 2 shows the result of these attempts. The electrode there depicted was in continual use for a month, after which the stem broke. The weight of platinum was less than 5 grams.

To avoid the use of platinum, it might perhaps be possible to make the outer electrode of silver when it is used as the cathode. It is probable that the metals deposited on it might be removed after electrolysis by the method of graded potential, although experiments in this direction have not yet been made.

As is explained later (p. 392), the electrodes 1c and 2 are not suitable for solutions containing metals which very readily pass from one stage of oxidation to another, such as copper in ammoniacal liquids, iron, tin, &c. In this case, an anode with a smaller oxidation and stirring efficiency is necessary. The former is obtained by making the surface of the electrode much smaller. Fig. 3 shows the electrode which was designed for this purpose. It is made almost entirely of glass, the total weight of platinum being $1\frac{1}{2}$ grams.

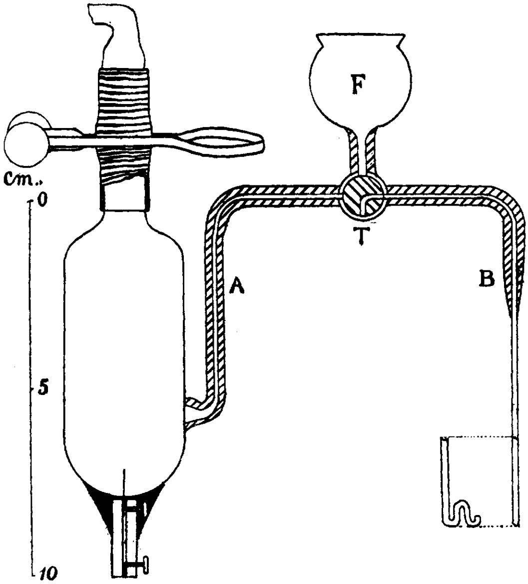

FIG. 5.

The Auxiliary Electrode.—The auxiliary electrode always used for the present investigation was a mercury-mercurous sulphate-$2N$ sulphuric acid electrode. As an auxiliary electrode has hitherto not been employed in analysis, a special form (Fig. 5) suitable for this purpose was designed. The distinctive feature of this electrode lies in the funnel *F* and connecting glass tube *A B*. It will be seen that the two-way tap *T* will allow the funnel *F* to be connected with either half of the glass tube *A B*, or will close all parts from each other. The half *A* permanently contains the 2*N*-sulphuric acid solution of the electrode. The half *B*, on the other hand, is filled for each experiment from the funnel *F* with a suitable connecting liquid, generally sodium sulphate solution. The end of *B* is made of thin tube of about 1½ mm. bore, and is bent round several times to minimise convection, as will be seen from the figure. While the electrode is in use, the tap, which must be kept free from grease, is kept closed, the film of liquid held round the barrel by capillary attraction making the electrical connexion, but towards the end of a determination a few drops are run out in order to expel any salt which may have diffused into the tube. The normal electrode is held in a separate stand so that it may easily be brought to or removed from the solution undergoing electrolysis.

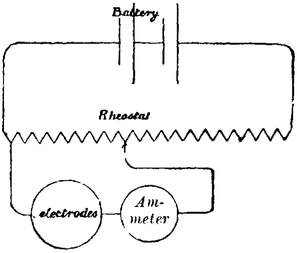

FIG. 6.

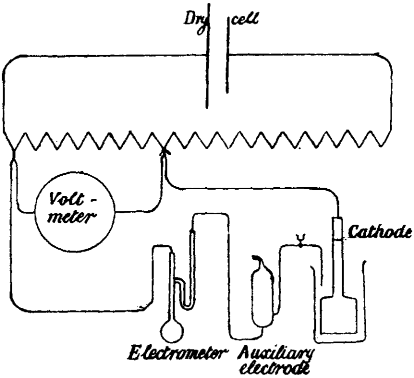

FIG. 7.

Electrical Connexions.—For separations by graded potential the electrical connexions must be made as shown in Fig. 6. The battery is connected directly to the two ends of a sliding rheostat, the electrolytic cell to one of them and the slider. It is manifestly essential that the sliding contact should be very good. A rheostat by Ruhstrat of Göttingen, with a carrying capacity of 15 amperes and a resistance of 2·6 ohms, proved very satisfactory. It was protected from the atmosphere of the laboratory by a coating of vaselin.

The arrangement (Fig. 7) adopted for the measurement of the potential difference auxiliary electrode-cathode is the one most usually employed at the present time in electrochemical research.

The electromotive force to be measured is balanced against a known electromotive force by means of a capillary electrometer. The known electromotive force is drawn from a sliding rheostat, the ends of which are connected with one or two dry cells. The value of the *E.M.F.* is read directly on a delicate voltmeter (range, 1·5 volts). For potential differences greater than 1·5 volts a Helmholtz 1 volt cell was interposed between the auxiliary electrode and the rheostat. The arrangement allows the voltage to be measured almost instantaneously, a matter of great importance in the present case. Owing to the very considerable advances that have been made in recent years in the construction of quadrant electrometers and their adjuncts, it seems probable that an electrometer might be permanently fitted up in such a manner as to be used as a direct-reading electrostatic voltmeter (range required, 1 volt; sensitiveness, 1 centivolt). If this were the case it would become as simple a matter to read the potential difference between the cathode and the electrolyte as that between the cathode and the anode.

Method of Carrying out an Experiment.—Where not specially stated to the contrary, the metal was always deposited on the outer electrode. To carry out an experiment the cathode, anode, and auxiliary electrode are placed in position, the electrolyte is heated to the required temperature and covered with a set of clock glasses having suitable openings for the electrodes. For the purpose of a separation the current is usually started at about 3—4 amperes and the potential of the auxiliary electrode noted. As a rule, this is only slightly above * the equilibrium potential. The current is then regulated so that the potential of the electrode may remain constant. When no by-reactions take place the current falls to a small residual value (generally about 0·2 ampere), as the metal to be separated disappears from the solution. The auxiliary electrode is then allowed to rise 0·1 to 0·2 volt, according to the metal.

It is obviously a matter of great importance to know when all the

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* In the present paper the author proposes to adhere to the following nomenclature. The potential of an electrode or of an auxiliary electrode is said to be higher in one case than in another when it opposes the passage of the current to a greater extent in the first than in the second case, and this irrespective of any consideration whether the actual value becomes greater or smaller as a result of the arbitrary nature of the conceptions positive and negative electricity. When, however, numerical values are stated these are always given with their correct sign, and the following abbreviations have been employed. The potential of the cathode (or anode) is the difference of potential between it and the auxiliary (2*N*-sulphuric acid) electrode. The potential of the auxiliary electrode is the difference of potential between it and the electrode undergoing measurement. A great deal of confusion unfortunately exists in contemporary literature, especially with regard to the sign o' potential differences, but the above nomenclature seems simple and rational.

metal has been deposited. Under the conditions just assumed the amount deposited per unit of time may be taken as roughly proportional to the amount still in solution.* This being so, it follows that the amount in solution will decrease in geometrical ratio during successive equal intervals of time. If we therefore make the safe assumption that the concentration of the metal has fallen to under 1 per cent. of its original value in the time during which the potential and the current have been brought to their final value, it is clear that by continuing the experiment half as long again, the concentration of the metal will fall to under 0·1 per cent., so that the deposition can then be considered finished.

In cases where by-reactions occur, the current does not fall to zero, but it generally attains a constant value which allows one to see when all the metal has been removed. In certain cases, the absence of the latter can be roughly tested for chemically, and by continuing the experiment for about half as long again as this reaction demands, the metal may be safely assumed to have been deposited completely. This method may be adopted, for example, in the separation of lead from cadmium, the former being roughly tested for by sulphuric acid. If none of these methods is available, the metal must be deposited to constant weight or else the separation must be carried out under very carefully defined conditions for a length of time proved more than sufficient by previous experiment.

Interrupting an Experiment.—A short time before completing the analysis, the inside of the tube 1_6, the sides of the beaker, and the clock glasses are washed by the aid of a wash-bottle and a few drops of liquid run out of the connecting limb of the auxiliary electrode. To interrupt the experiment, the auxiliary electrode and the clock glasses are removed, the tripod is then taken from under the beaker and the latter lowered until the surface of the liquid is just below the outer electrode. During this time the latter is washed. The stirrer is now stopped before lowering the beaker any further. The latter is then replaced by a slightly larger one, the tripod put back, and the electrode again washed. It is then disconnected, shaken, dipped first into a jar containing alcohol, shaken, then into another containing ether, and then dried for about half a minute over a Bunsen burner. The collar *A* is carefully dried by a silk cloth before weighing. The

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* This is based on the supposition that the concentration of metal in the layer of liquid touching the electrode is kept practically at zero during the whole of the experiment (see Brunner, *Zeitsch. physikal. Chem.*, 1903, **47**, 56). When this is not the case, the first stages of the separation are somewhat protracted, and if the duration of the whole experiment is made to conform with them, it therefore becomes a little longer than absolutely necessary, a matter which is, of course, of no importance for the result.

remaining liquid is washed into the larger beaker and is then ready for the deposition of the next metal.

When only one metal is contained in the solution undergoing analysis, it is simpler to stop the stirrer, take away the beaker, and replace it by two successive ones containing distilled water. In both cases the current is left on during the process of interruption.

The beaker in which the first deposition of a separation is carried out was only slightly wider than the electrode and the amount of liquid roughly 85 c.c. In the second separation the amount was usually 130 c.c. and so on.

The rate of stirring varied very considerably from one experiment to another without greatly affecting the result. It may be taken as having been between the limits of 300 and 600 revolutions per minute.

Conditions for Obtaining Adherent Metal Deposits.

In electroanalytical experiments the question of obtaining firmly adherent deposits continually presents itself. This matter has been treated in several recent American papers (Bancroft, *J. Physical Chem.*, 1905, **9**, 277 ; Snowdon, *Trans. Amer. Electrochem. Soc.*, 1905, **7**, 143; Betts, *Trans. Amer. Electrochem. Soc.*, 1905, **8**, 63). A noteworthy discussion on the theory of the inclusion of metalloids and other phenomena occurring during metal deposition is also due to Jordis (*Zeitsch. Elektrochem.*, 1905, **11**, 787).

1. *Uniform Distribution of the Deposit over the Electrode.*—This is a matter which, apart from the shape of the electrode, depends solely on the relation between polarisation (in its broadest sense) and the electromotive force required according to Ohm's law to drive the current from one part of the liquid to another. It has been discussed by the author in some detail (*Zeitsch. Elektrochem.*, 1904, **10**, 452). The case of metals, such as cadmium and zinc, requiring a higher potential for their precipitation from the majority of their solutions than hydrogen should also be discussed here. These metals can only be deposited in virtue of the supertension, required to liberate the hydrogen as a gas. This supertension varies according to the material of the electrode, and even according to the state of its surface in various parts. It may therefore happen that the metal is deposited on a part of the electrode with a high supertension and continue to grow there, whilst at rougher parts of the electrode only hydrogen is evolved. Some solutions appear to be more sensitive to these variations in the quality of the electrode than others. Thus, in the case of zinc, a beautiful uniform deposit was once obtained from a boiling ammoniacal solution, but on repeating the experiment the precipitate obtained was patchy and useless.

2. *The Actual Nature of the Deposits.*—These may be classified as spongy, coarsely crystalline, and finely crystalline. Only the last-named are in general suitable for the purposes of the analyst.

Spongy deposits are probably in most cases due to the fact that the metal has been primarily produced in the form of an unstable compound, generally a hydride which has subsequently decomposed with the evolution of gas. A typical instance of this is afforded by bismuth. Depositions of this metal in an adherent form by slow methods have been described by Wimmenauer (*Zeitsch. anorg. Chem.*, 1901, **27**, 3); Brunck (*Ber.*, 1902, **35**, 1871); Kammerer (*J. Amer. Chem. Soc.*, 1903, **25**, 83). The real condition necessary for the production of a dense deposit was, however, understood by none of these experimenters. Consequently they give details of current strength, voltage, &c., which in their turn depend to a very great extent on the apparatus employed and on the amount of convection which may take place during the determination. It thus happened that Fischer and Boddaert (*loc. cit.*), working in the Aachen laboratory, failed to repeat their experiments. As will be seen from the present paper, bismuth can be obtained in an adherent form from nearly any solution, if only the potential of the cathode is kept low enough to prevent the formation of a hydride. If the potential of the electrode is not kept under control, the general conditions which keep it low and thus cause the production of a dense deposit are vigorous circulation of the electrolyte, small current density, and the presence of an oxidiser (nitric acid), and these conditions have been empirically employed to a greater or smaller extent by those investigators who have hitherto been successful in the deposition of bismuth. Copper behaves in a manner similar to bismuth, although in its case the phenomena are much less marked.

In certain cases, the precipitation of a metal hydroxide due to hydrolysis in consequence of the impoverishment of the solution in the layer of liquid adjacent to the electrode may also give the deposit a spongy appearance (see Bancroft, *loc. cit.*).

All the conditions discussed later, which may be considered to hasten the transformation of an unstable into a stable form, are also found to militate against the formation of spongy deposits.

The majority of electrolytic metal deposits are crystalline in structure, and may be either coarse- or fine-grained. The former are apt to lead to the formation of trees, from causes which must be classified under (1), and are usually loose; the latter are the deposits which are most desirable from the plater's point of view.

In considering the question of the fine-grainedness of a metal deposit, Bancroft (*loc. cit.*) has adopted a view originally put forward by Pfanhauser (*Galvanoplastik*, p. 73), that the crystallisation of electrolytic metal coatings is analogous to the crystallisation of salts from solution, and in the elaboration of this view he comes to the conclusion that a high current density and potential difference, a low temperature and the presence of colloids favour a fine-grained deposit. Some of these views have been experimentally verified by Snowdon.

With regard to these views the author of the present paper wishes to make the following additional remarks. The production of crystals is in almost all cases bound up with the intermediate formation of a metastable state. Thus crystallisation from a solution is probably always connected either with local supersaturation or with the intermediate production of an under-cooled liquid. In a similar way, it seems very probable that metal deposits are produced electrolytically in the first instance in a metastable state, and that it depends on the ease and rapidity with which this state is destroyed whether a fine- or a coarse-grained deposit is to be the ultimate result. This view comprises that recently put forward by E. Müller and Bahntje (*Zeitsch. Elektrochem.*, 1906, **12**, 317), that metals are deposited in the first instance in a colloidal state. The general conditions that would, on the author's view, favour a dense deposit are therefore the same as those put forward by Bancroft. Of these, experience shows that a high potential of the electrode is by far the most important. The reasons of analogy advanced by Bancroft for the favourable effect of a low temperature on the density of the deposit, however, appear to be inapplicable and not to be borne out by experience.

When colloids are present in the solution, these are often deposited with the metal (see Müller and Bahntje, *loc. cit.*) and effectually hinder crystallisation. The metal may thus be precipitated in a beautifully burnished condition. In the present investigation, copper was in one experiment obtained in a beautifully burnished state of the appearance of bronze by the electrolysis of a cold solution containing a large amount of ammonium acetate, the weight being about 2 per cent. too high. The explanation is probably to be sought in the presence of colloidal substances, either owing to accident or to the action of the current on the acetate.

EXPERIMENTAL.

Silver.—The precipitation of silver for analysis was studied in nitric acid, acetic acid, ammoniacal and potassium cyanide solutions. One of the difficulties encountered in nitric acid solutions consists in the formation of silver peroxide on the anode. Owing to the instability of this compound at higher temperatures, it is, therefore, possible to avoid its production by maintaining the solution at boiling temperature. The silver is then obtained as a uniform and coarsely crystalline, white deposit. It is, however, somewhat loose, and in consequence the results are not trustworthy when large quantities have to be precipitated. In separations of traces of silver from other metals the method could probably be employed with advantage. Several determinations were carried out in which more than half a gram of silver was deposited with an error of about 3 milligrams. The solutions contained between 1 and 2 c.c. of strong nitric acid per 85 c.c., and a current strength starting at 3 amperes and falling to 0·2 ampere was employed in such a manner that the auxiliary electrode showed a potential below 0·10 volt.

For the purpose of separations from other metals the method may in certain cases be improved by coating the cathode with mercury and thus obtaining the silver as an amalgam. This amalgam is adherent only when in a semi-liquid state, and in consequence it is necessary to employ at least ten times as much mercury as silver. The experiments were carried out with the potential of the cathode regulated to a minimum as if a separation from other metals were being effected. For reasons explained later (p. 389), it is therefore essential to keep the solution at the boiling point. Tartaric acid was added, as this reagent is required in some of the separations. The method of drying the electrode was the same as that used for mercury (see later). The following result was obtained under these conditions.

Experiment.—The electrode was coated with about 1·5 grams of mercury. The solution contained 0·2332 gram of mercury as nitrate, 18 grams of tartaric acid, and 1 c.c. of concentrated nitric acid per 85 c.c. During electrolysis it was observed to become turbid and finally clear.

Ag taken.	Ag found.	Amps.	Volts, auxiliary.	Temp.	Time in minutes.
0·1078	0·1072	7—0·2	0—0·15	boiling	7

As silver is deposited from acetic acid solutions containing a large amount of acetates at a higher potential than from nitrate solutions (in consequence of the small number of Ag ions present), it was to be expected according to the general considerations advanced above that a more finely crystalline, and therefore firmer, precipitate would be obtained. This proved to be the case, the silver deposit remaining unaltered by tapping, and almost so by scraping with a horn spatula. In consequence, the results obtained were sufficiently good to make the method suitable for analysis. The following experiments were carried out.

Experiments.—In Nos. 1, 2, 3, and 5, silver was deposited on the electrode, weighed, and dissolved in a solution of 5 c.c. of concentrated nitric acid; 25 grams of ammonium acetate were then added and the solution was heated to boiling, the burner being removed during deposition. In experiment 4 the electrolyte contained a known quantity of silver nitrate solution analysed according to the ammonia method (see later), to which 5 c.c. of concentrated nitric acid and 20 grams of ammonium acetate were added

No.	Ag taken.	Ag found.	Amps.	Volts between anode and cathode.	Temp.	Time in minutes.
1.	0·5373	0·5365	3·5—0·2	1 —1·3	boiling	8
2.	0·5363	0·5361	3·5—0·2	1 —1·3	,,	8
3.	0·5361	0·5358	4 —0·2	1 —1·3	,,	7
4.	0·5389	0·5397	3 —0·2	1 —1·2	,,	6
5.	0·5397	0·5399	5 —0·2	1·1—1·2	,,	6

As silver is deposited from ammoniacal solutions at a higher potential than from acetate solutions, it was expected that a still firmer deposit would be obtained, and this proved to be the case. The deposits were unattacked by both tapping and scraping. The solutions were kept boiling vigorously during deposition. As there are practically no sources of error apparent in this method, the results obtained by it are probably always exceedingly trustworthy. The following experiments were carried out.

Experiments 1, 2, 3.—The silver was deposited on the cathode, weighed, and dissolved in acid containing 10 c.c. of concentrated nitric acid. Fifteen c.c. of concentrated ammonium hydroxide were then added :

No.	Ag taken.	Ag found.	Amps.	Volts between anode and cathode.	Temp.	Time in minutes.
1.	0·5371	0·5371	3—0·2	1—1·3	boiling	8
2.	0·5371	0·5373	5—0·2	1—1·3	,,	7
3.	0·5354	0·5352	4—0·2	1—1·3	,,	7

Silver is precipitated from alkaline cyanide solutions at a much higher potential than from the foregoing, and accordingly leaves nothing to be desired as regards density of the deposit. Nevertheless, there are undoubtedly more sources of error in this method than in the others, as alkaline solutions containing organic substances appear to cause difficulties due to the decomposition products formed at the anode (see p. 401). Exner (*loc. cit.*) obtained correct results for silver from cyanide solutions, but Fischer and Boddaert (*loc. cit.*) consistently obtained numbers about 0·5 milligram low. The following are the results obtained in the present investigation.

Experiments.—In No. 1 metallic silver was deposited on the electrode, weighed, and dissolved in an acid solution containing 3 c.c. of concentrated nitric acid; the latter was neutralised with ammonia and about 2·5 grams of potassium cyanide were added, the temperature being about 90°. Experiment 2 was as 1, but the quantities were 15 c.c. of concentrated nitric acid, neutralised by ammonia and 4 grams of potassium cyanide. In experiment 3 a measured volume of silver solution was used together with 5 c.c. of concentrated nitric acid, 3⅓ grams of sodium hydroxide, and 3 grams of potassium cyanide:

No.	Ag taken.	Ag found.	Amps.	Volts * anode–cathode.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·5389	0·5361	8—5	3·5	—	90°	6
2.	0·5361	0·5340	10—9	3·8—3·9	—	90	6
3.	0·2694	0·2699	3—0·2	—	1·15—1·25	60	9

* Rough values.

Mercury and its Separation from Silver.

One of the chief differences from the analyst's point of view between the electrolytic determination of mercury and that of other metals lies in the manner of drying which must be adopted in consequence of the volatility of this metal. The method usually recommended consists in placing the wet electrode in a vacuum desiccator. As it was realised that a great part of the advantage resulting from rapid deposition is lost if a lengthy drying process is employed, several experiments were carried out with the object of shortening this operation. A current of dry air was drawn over the electrodes; the latter, however, always lost weight. Air saturated with mercury vapour was then tried both hot and cold. In the former case the electrode gained in weight, in the latter it remained constant. Thus 0·6241 gram of mercury was deposited on the cathode, dried, weighed, then dipped into water, allowed to drain on filter paper for a few minutes, and dried for an hour and a half according to the above method. The weight found was 0·6242 gram. The apparatus employed is shown in the accompanying Fig. 8, and will need no further explanation. The time varied in different experiments between forty minutes and two hours. The electrode was always dried until constant in weight.

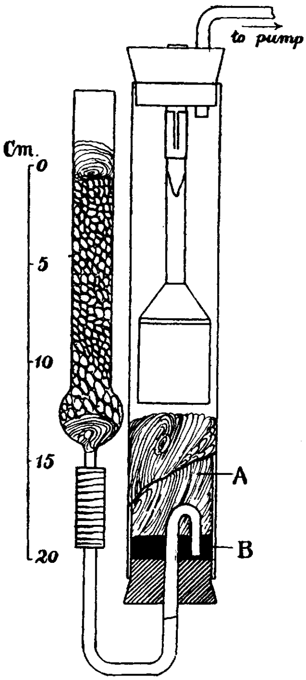

Fig. 8.
A. Cotton wool.
B. Mercury.

It is well known that mercury may be deposited from nitrate solutions either in loose drops unsuited for weighing or as a mirror, but so far as I am aware it has never been pointed out that the former always occur at first during deposition while the potential of the cathode is low, and it is only when the potential rises and hydrogen is given off that the mercury spreads out as a mirror.

From ammoniacal and cyanide solutions the mercury is precipitated in exceedingly fine drops which adhere to the electrode sufficiently for their quantitative estimation.

When nitrate solutions are employed in quantitative separations by graded potential from metals such as copper and bismuth, it is manifestly impossible to allow the potential of the cathode to rise to the value at which a bright mirror is formed. In order to obtain deposits sufficiently adherent for quantitative purposes, it is in this case essential to keep the solution boiling during deposition. In Exner's experiments the solution was maintained at a temperature slightly below 100°. Fischer and Boddaert, however, obtained too low results working according to this method, and state that it is necessary to keep the electrolyte at the ordinary temperature. Owing to the very appreciable volatility of mercury at high temperatures, there must always be considerable risk of loss if hydrogen is generated rapidly on the surface of the electrode in a hot solution. In separations by graded potential in which there is no possibility of the production of hydrogen, this objection to high temperatures obviously does not hold. In all cases, great care was taken to keep the surface of the mercury covered completely by the electrolyte.

The amount of mercury which may be precipitated on the gauze electrode is very considerable, 2 to 3 grams having been deposited in a form sufficiently adherent to prevent any possibility of loss by vigorous shaking. For the purpose of weighing, the electrode was suspended to the balance by a wire. An objection to the use of the gauze electrode should be stated here. It is the very considerable loss in weight which the gauze undergoes when the mercury is removed. It amounted, as a rule, to about 3 milligrams. This objection would be largely overcome if it were possible to obtain gauze commercially made of platinum-iridium instead of platinum wire. The following determinations were carried out:

Experiments 1 *and* 2.—A weighed quantity of mercury was dissolved in nitric acid, evaporated to dryness on the water-bath, nitric acid added and made up to a known volume. Of this solution measured quantities were taken. The amount of free nitric acid present in the solution amounted to about $1\frac{1}{2}$ c.c. per 85 c.c.:

No.	Hg taken.	Hg found.	Amps.	Volts anode-cathode.	Temp.	Time in minutes.
1.	0·5830	0·5833	9	2·6—3·7	warm	5
2.	0·5830	0·5831	9	—	,,	5

Experiment 3.—Ammonia method with limited potential; 10 c.c. of concentrated nitric acid and 20 c.c. of concentrated ammonium hydroxide were added to the solution, which was heated nearly to boiling during electrolysis:

Hg taken.	Hg found.	Amps.	Volts auxiliary.	Time in minutes.
0·4665	0·4672	3—0·2	0·40—0·50	6

Separation from Silver.—As mercury is deposited from most solutions at almost the same potential as silver, it seems hopeless to effect a separation by graded potential. In the books on electro-analysis it is stated that the two may be deposited together and the mercury expelled by ignition. Details are, however, not given. As a temperature above the melting point of silver is said to be necessary for the complete decomposition of silver-amalgam (Gay-Lussac, see Dammer, *Handb. Anorg. Chem.*, 2, 943), it was thought undesirable, to endanger the electrode by experiments in this direction. The metals were therefore deposited together, dissolved in nitric acid, and separated by the cyanide method. The pure silver cyanide thus obtained was dissolved in potassium cyanide and analysed by electrolysis. An experiment in which the combined nitrates of silver and mercury were evaporated to dryness and ignited strongly in a porcelain crucible in the hope that only pure silver might be left behind, failed owing to the formation of a mercury compound with the glaze of the crucible.

Experiment.—The cathode was plated with about 1·5 grams of mercury (see p. 386), weighed, and the mercury and silver deposited into this from a boiling solution containing 1 c.c. of concentrated nitric acid and 18 grams of tartaric acid (the latter was added as it was thought that its presence might probably be required in later separations from other metals). After weighing, the combined metals were dissolved in a boiling solution containing 20 c.c. of concentrated nitric acid; the liquid was then made alkaline with sodium hydroxide faintly acid with nitric acid and potassium cyanide added to it until it was clear. It was then warmed slightly and the silver precipitated by nitric acid, allowed to settle and collected. The filter paper with the silver cyanide was then added to a solution containing about 3·5 grams of potassium cyanide, and the silver deposited at about 80° with a current of 3 amperes; the stirrer was kept moving slowly to prevent too great disintegration of the paper.

Hg+Ag taken.	Hg+Ag found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
0·4488	0·4486	5—0·2	0—0·10	boiling	14

Ag taken = 0·2156 Ag found = 0·2132

Copper and its Separation from the preceding Metals.

No difficulty was experienced in depositing copper from nitrate and sulphate solutions. As is known, a smooth deposit is obtained from nitric acid solutions, whereas the copper produced in solutions containing only sulphuric acid is usually slightly powdery at the end of the experiment. This is no doubt due to the intermediate formation of a copper hydride, when the potential rises to the value at which hydrogen is evolved. In solutions containing nitric acid or other oxidising agents this cannot take place, as reduction first sets in. Even from sulphuric acid solutions smooth deposits may be obtained if the metal is deposited at a limited potential of the cathode. A slightly powdery surface of the deposited copper does not appear to cause loss in washing, and thus does not affect the accuracy of the results. The loss in washing in solutions containing free nitric acid also appears to be negligible, so long as oxides of nitrogen are absent. When, however, these were present even in traces after the solution of metallic copper in nitric acid, it was found necessary to add an alkali acetate to the solution before disconnecting. The following results were obtained :

Experiments.—Metallic copper was deposited on the electrode from an acid sulphate solution, weighed, dissolved in a solution containing 2·0 to 2·5 c.c. of concentrated nitric acid, redeposited, and 5 grams of sodium acetate (No. 1) or 7 grams of ammonium acetate (Nos. 2 and 3) added before disconnecting :

No.	Cu taken.	Cu found.	Amps.	Volts anode-cathode.	Temp.	Time in minutes.
1.	0·2939	0·2938	10	2·5	warm	6
2.	0·2504	0·2506	10	2·8	,,	6
3.	0·2504	0·2505	10	2·6	,,	6

For the following experiments, either measured quantities of a copper sulphate solution or weighed quantities of copper sulphate crystals (Kahlbaum) were taken, the amount of copper in both having been previously estimated according to the method proved correct by Nos. 1, 2, 3. In Nos. 4 and 5, 1 c.c. of concentrated nitric acid, in No. 6, 1 c.c. of concentrated sulphuric acid, in Nos. 7, 8, and 9, 0·75 c.c. of concentrated sulphuric acid were added. In No. 9 the free mineral acid was removed by ammonium acetate before disconnecting :

No.	Cu taken.	Cu found.	Amps.	Volts anode-cathode.	Temp.	Time in minutes.
4.	0·2474	0·2471	10	2·8	lukewarm	6
5.	0·2243	0·2239	10	—	hot	6
6.	0·2474	0·2476	10	3·0	lukewarm	6
7.	0·2949	0·2953	10—7	2·9—3	boiling	5
8.	0·2690	0·2693	10	2·8—3·2	hot	5
9.	0·2520	0·2517	10	2·8	boiling	7

As far as can be judged from the experiments carried out, the electrolysis of copper solutions containing free acetic acid and a considerable quantity of alkali acetates does not give accurate results. In some cases, values 1½—2 per cent. too high (5 milligrams) were obtained. In other cases (see experiments on separation from silver) the results were better.

From boiling tartrate solutions, correct results for copper have been repeatedly obtained at limited potential. The copper is all deposited at a potential of the $2N$-sulphuric acid electrode below 0·60 volt.

Experiment.—2½ c.c. of concentrated nitric acid, 10 grams of sodium tartrate, volume 120 c.c. :

Cu taken.	Cu found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
0·2941	0·2927	3—0·2	0·45—0·55	100°	10

A difficulty arose in the experiments in ammoniacal solutions from the ready transformation of cuprous to cupric compounds and *vice versâ*, the anode effecting the former, the cathode the latter reaction. In consequence, the potential of the cathode does not rise high enough to allow all the copper to be deposited. Similar difficulties are met with frequently in electrolysis in the case of such metals as iron and tin, and to a very much smaller extent in the case of mercury. There appear to be three different principles by the application of which the difficulty may be met: (1) by the use of a diaphragm; (2) by the addition of reducing agents which may be oxidised at the anode in place of the whole or part of the salt undergoing electrolysis; (3) by lowering the oxidising and stirring efficiency of the anode. This can be done by making use of the anode depicted in Fig. 3 on p. 377.

The first method would be the most efficient, and would undoubtedly, if it were found possible to carry it out in a practicable manner, eliminate most of the difficulties which are still met with in electro-analysis.

The second principle comes into operation where solutions of oxalates, &c., are employed.

The third was found sufficient in the present case. The following experiments were carried out:

Experiments.—In Nos. 1 and 2 the following were added to the electrolyte, 1 gram of ammonium nitrate, 20 c.c. of concentrated ammonia solution; in No. 3, 10 c.c. of concentrated nitric acid and 17 c.c. of concentrated ammonia solution. The copper deposit was slightly discoloured:

No.	Cu taken.	Cu found.	Amps.	Volts anode–cathode.*	Temp.*	Time in minutes.
1.	0·2941	0·2937	3—5	4·5	20—50°	9
2.	0·2941	0·2937	3—5	4·5	20—50	10
3.	0·3682	0·3682	—	—	80	20

* Rough values.

Separation from Silver and Mercury.—Both silver and mercury can be deposited completely from nitrate solutions at a potential of the 2*N* sulphuric acid electrode below 0·10 to 0·15 volt, and as copper does not begin to be precipitated below 0·30 volt a separation can be readily effected. (For the conditions governing the adherence of deposits, see pp. 385, 389.)

Experiments 1 *and* 2.—About 0·75 c.c. of concentrated nitric acid per 85 c.c. :

No.	Taken.	Found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·5330 Hg	0·5850 Hg	10—0·2	0·0—0·15	boiling	6
	0·2465 Cu	0·2467 Cu	9	—	warm	5
2.	0·5830 Hg	0·5846 Hg	10—0·2	0·0—0·15	boiling	6
	0·2465 Cu	0·2469 Cu	—	—	—	—

Silver was separated from copper in boiling acetate solutions, both by the aid of an auxiliary electrode, the potential of the latter being kept less than 0·30 volt, and also by simply regulating the potential difference between the anode and the cathode below 1·25 volts. Before disconnecting, care must be taken to reduce the voltage sufficiently to preclude its rising above the fixed value during the operation.

Experiments.—In Nos. 1 and 2, the solution contained 5 c.c. of concentrated nitric acid and 25 grams of ammonium acetate; in No. 3, 4 c.c. of concentrated sulphuric acid and 25 grams of sodium acetate; in No. 4, 4 c.c. of concentrated nitric acid and 25 grams of sodium acetate. In experiment 4, 6 to 7 c.c. of concentrated nitric acid were added before depositing the copper:

No.	Taken.	Found.	Amps.	Volts anode-cathode.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·5389 Ag	0·5394 Ag	2·5—0·4	1·0—1·25	—	boiling	9
	0·155 Cu	—	—	—	—	—	—
2.	0·5389 Ag	0·5386 Ag	2·8—0·5	1·0—1·20	—	boiling	7
	0·0990 Cu	0·0994 Cu	4	3	—	hot	4
3.	0·5389 Ag	0·5389 Ag	2·8—0·8	1·0—1·20	—	boiling	7
	0·2474 Cu	0·2483 Cu	6—3	2·6	—	hot	5
4.	0·2695 Ag	0·2705 Ag	2·7—0·4	—	0·30	boiling	—
	0·5882 Cu	0·5908 Cu	10	3·5	—	tepid	—

Silver may also be separated from copper in ammoniacal solutions with the aid of the auxiliary electrode if the potential of the latter be kept below 0·50 volt. As will be clear from the remarks on p. 392, the anode, Fig. 3, must be employed. It will also be understood that after complete deposition of the silver the current does not fall to zero. The absence of the latter must therefore be confirmed by means of hydrochloric acid.

Experiments.—10 c.c. of concentrated nitric acid, 15 c.c. of concentrated ammonium hydroxide solution;

No.	Taken.	Found.	Amps.	Volts anode-cathode.*	Volts auxiliary.	Temp.	Time in minutes.
1.	0·2170 Ag	0·2163 Ag	3—1·3	2	0·38—0·50	boiling	10
	0·3682 Cu	0·3680 Cu	4	5·4	—	warm	10
2.	0·2170 Ag	0·2165 Ag	5—1·5	3·5	0·45—0·50	boiling	9
	0·3682 Cu	—	—	—	—	—	—

* Rough values.

Bismuth and its Separation from all the preceding Metals.—As has already been pointed out, the precipitation of bismuth as such in a coherent form suitable for analysis has hitherto been considered one of the most difficult electroanalytical operations, and a satisfactory method can hardly be said to have been available.

In the present investigation, satisfactory results were obtained in acetate, tartrate, and nitrate solutions; the only condition which had to be observed was to keep the potential of the electrode as low as possible. A temperature of about 60° was found the most suitable. In solutions containing free nitric acid, the potential of the cathode is automatically kept low owing to the reduction of the acid if only the stirring efficiency is sufficient to prevent its local exhaustion. With the present electrodes it was found possible to use currents of 2 to 3 amperes without any further precaution, in contradistinction to the results obtained with different apparatus by other investigators. When tartrate and acetate solutions were employed, it was found necessary to keep the potential of the cathode carefully under control by means of the auxiliary electrode as described on p. 381. The following experiments were carried out:

Experiments 1 *and* 2.—Bismuth was deposited on the electrode from a nitrate solution, weighed, dissolved in an acid solution containing 2½ c.c. of concentrated nitric acid, then 8 grams of sodium tartrate were added. At the end of the experiment, before disconnecting the solution was made alkaline with 5 c.c. of concentrated ammonium hydroxide:

No.	Bi taken.	Bi found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·2184	0·2187	3—0·2	0·63—0·9	warm	9
2.	0·2999	0·2996	3—0·2	0·63—0·9	,,	9

A solution was then made up by dissolving approximately 14 grams of bismuth oxide (Kahlbaum) in a litre of acid containing approximately 100 c.c. of concentrated nitric acid. This solution was analysed according to the method proved correct by experiments 1 and 2 (two determinations, difference 0·3 milligram). Measured quantities of this solution were taken for the following experiments with the exception of Nos. 8, 11, and 12. In experiments 3—6, the solution contained about 2½ c.c. of concentrated nitric acid in 85 c.c.; the same electrolyte was employed in experiment 7, but neutralised with ammonia before disconnecting. In experiment 8, electrolytically deposited bismuth was dissolved in 2½ c.c. of concentrated nitric acid, then 10 grams of ammonium acetate added, and the cathode potential kept under control. In experiment 9, the electrolyte contained 10 c.c. of formaldehyde, but was otherwise identical with that of No. 7. In experiments 10—13, 2½ grams of concentrated nitric acid and 8 grams of sodium tartrate were present, and the solution was neutralised with sodium hydroxide before disconnecting; metallic bismuth formed the starting point in Nos. 11 and 12. In experiment 14, the solution contained 2½ grams of concentrated nitric acid and 12 grams of sodium tartrate:

No.	Bi taken.	Bi found.	Amps.	Volts anode-cathode.	Volts auxiliary.	Temp.	Time in mins.
3.	0·3223	0·3207	3—2	2·4	—	cold	8
4.	0·3223	0·3215	3	2·1—2·9	—	,,	11
5.	0·3223	0·3208	3	—	—	,,	11
6.	0·3223	0·3212	3	—	—	,,	12
7.	0·3223	0·3226	3—2	2·1—3·0	—	,,	9
8.	0·3207	0·3199	3·5—0·4	2·7	0·65—0·80	tepid	11
9.	0·3203	0·3198	4—0·2	—	0·65—0·80	,,	10
10.	0·3223	0·3216	2—0·2	2·4—1·9	0·65—0·90	cold	15
11.	0·3216	0·3203	2—0·2	—	0·65—0·90	,,	13
12.	0·3198	0·3194	2—0·2	—	0·65—0·90	,,	—
13.	0·2395	0·2389	3—0·2	—	0·63—0·75	hot	—
14.	0·3886	0·3882	3—0·2	1·3	0·65—0·70	boiling	11

Several determinations of bismuth as amalgam were also carried out, error 0·7—0·8 milligram on 0·2 gram of bismuth. The method requires far more time and trouble than the direct estimation and is probably less accurate than that of experiments 1 and 2.

Separation from the preceding Metals.—In the electropotential series for acid solutions, bismuth stands about 0·1 to 0·2 volt higher than copper, and can therefore be separated from silver and mercury in acid solution by the same methods as the former metal. Its separation from copper is, however, somewhat difficult in consequence of its close proximity to this metal. In nitric acid solutions the difference between the deposition potentials of the two metals is only about 0·10 volt, and a separation is quite impracticable. In boiling tartrate solutions containing free tartaric acid, copper is deposited at a potential between 0·40 and 0·60 volt and bismuth between 0·60 and 0·70 volt. As a result it is found that a separation by graded potential may be effected if the quantity of bismuth is very small by maintaining the potential of the auxiliary electrode below 0·60 volt. When, however, the quantity of bismuth is large, some of it is deposited with the copper, and must be separated from it by dissolving the metal in nitric acid and repeating the operation.

Experiments.—The solutions contained about 2½ c.c. of concentrated nitric acid and 10 grams of sodium tartrate. The copper depositions were repeated, the auxiliary electrode being maintained at 0·60 volt for two minutes in each. The numbers in brackets are the results of the first deposition :

No.	Taken.	Found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·2941 Cu	0·2929 (0·3033)	4—0·1	0·50—0·60	boiling	8
	0·3223 Bi	0·3221 Bi	4—0·2	0·60—0·80	hot	6
2.	0·2941 Cu	0·2926 (0·2993)	5—0·2	0·50—0·60	boiling	9
	0·3223 Bi	—	—	—	—	—

Another method of separating copper from bismuth has been suggested by E. Smith (*Amer. Chem. J.*, 1890, **12**, 428). It consists in preparing an alkaline solution of the two metals and adding potassium cyanide, thus converting the copper into a double cyanide, a compound which requires a very high potential for its decomposition. The bismuth does not form a cyanide, and can be deposited at a much lower potential. Smith recommends the use of a current of 0·2 ampere, and required nine hours for a separation.

Methods of separation with a fixed current strength, being devoid of a scientific basis, can, however, not be considered trustworthy. Satisfactory results may, on the other hand, be obtained by keeping the potential of the cathode under control. In the present case, the auxiliary electrode was kept below 1·40 volts. It was found necessary to use a hot solution and to prevent the formation of a deposit of bismuth pentoxide on the anode by the addition of formaldehyde. The bismuth was kept in solution by means of an alkali tartrate.

Experiments.—Copper and bismuth were deposited in weighed quantities on the cathode and dissolved in a boiling solution of 3 c.c. of concentrated nitric acid. Then 8 grams of sodium tartrate, 3 grams of sodium hydroxide, 5 grams of potassium cyanide, and 10 c.c. of formaldehyde were added. The current was kept low enough to prevent the blue colour of the alkaline copper tartrate from making its appearance (due to the decomposition of the potassium cyanide). The bismuth was taken to constant weight :

No.	Taken.	Found.	Amps.	Volts anode-cathode.*	Volts auxiliary.	Temp.	Time in minutes.
1.	0·3886 Bi	0·3871 Bi	2—0·2	0·4	1·08—1·40	roughly 80°	36
	0·2995 Cu	0·2990 Cu	10	3·5	—	boiling	8
2.	0·2503 Bi	0·2498 Bi	1·5—0·2	0·5	1·10—1·40	roughly 80°	23
	0·3590	0·3585	10	3·6	—	boiling	9

* Rough values.

Lead and its Separation from all the preceding Metals.—Lead may be determined both in the form of peroxide and as metal. In the form of peroxide its adherence to the electrode was found to depend greatly on temperature. In the cold it is very loose, and only small currents may be employed. When deposited from a boiling solution it is, however, exceedingly adherent, as has already been found by Exner, but a considerable strength of current must be used to counteract the solvent action of the acid. In the present investigation, it was deposited both on the inner and on the outer electrode. In the former case it was found desirable not to use very large quantities. The temperature chosen was about 60°.

Experiments.—A weighed quantity of pure lead (Kahlbaum) was dissolved in nitric acid, boiled to expel nitrous fumes, and made up to a known volume.

In experiment 1 the electrolyte contained 10 c.c. of concentrated nitric acid; in experiments 2—5, 15 c.c. of concentrated nitric acid per 85 c.c. The peroxide was deposited on the outer electrode in Nos. 1—3, on the inner electrode in Nos. 4 and 5. It was dried in the usual way at 200°:

No.	Pb taken.	Pb found as PbO_2.	Amps.	Volts anode-cathode.	Temp.	Time in minutes.
1.	0·1383	0·1374	3	2·4	roughly 60°	7
2.	0·3457	0·3465	3	2·2	,,	9
3.	0·3457	0·3455	3	2·2	,,	9
4.	0·1383	0·1365	2	2	,,	9
5.	0·1383	0·1384	2	2	,,	10

Lead may also be deposited as metal either in a faintly acid, an ammoniacal, or an alkaline solution, when reducing agents are added to prevent the formation of the peroxide. The reducing agent employed was either tartaric acid or glucose, and the solution was kept hot (see the experiments on the separation of lead from bismuth and from cadmium, pp. 399 and 402). The deposit is roughly crystalline and not very firm when obtained from an acid solution. It is denser when produced in an ammoniacal and still denser in an alkaline solution, corresponding to the potential of the electrode at which it is formed (see general considerations, p. 385).

Separation from the preceding Metals.—The separation of lead from other metals based on the fact that it can be deposited on the anode as peroxide is well known; the present electrodes, however, allow simplifications and improvements to be made in some cases. When it is desired to separate lead from a metal such as copper, there is no need to acidify the solution strongly with nitric acid in order to prevent the deposition of metallic lead if only the quantity of the copper is so great that all the lead is deposited on the anode a considerable time before exhaustion of the copper sets in. Thus an experiment was successfully carried out in which lead and copper were deposited in one operation from a solution containing sulphuric and nitric acids. A precipitate of lead sulphate was present, which, however, dissolved as the lead was deposited on the anode. It should be mentioned here that in certain other experiments attempts were made to separate metals from solutions containing precipitates which were not dissolved during the electrolytic operation. In nearly all such cases it was not found possible to wash the deposited metal free from the precipitate.

Experiment.—Measured quantities of the standardised copper sulphate and lead nitrate solutions were taken and 1 c.c. of concentrated nitric acid added. The solution was hot. A current of 2 amperes was passed for five minutes, during which all the lead sulphate disappeared and the liquid still remained blue. The current was then increased to 10 amperes and all the copper deposited. The inner electrode was the anode. The lead peroxide was not very adherent, but none was lost in washing :

Cu taken 0·2474 ; Cu found 0·2476.
Pb ,, 0·1383 ; Pb ,, 0·1386.

According to B. Neumann (*Analytische Elektrolyse der Metalle*, p. 176), the separation of lead as peroxide from silver is not trustworthy as the deposit is said frequently to contain small quantities of silver. Owing to the great instability of silver peroxide at 100° it was expected that if the solution were kept boiling during the deposition a quantitative separation could be effected, and this proved to be the case. The solutions employed were strongly acid. A small amount of silver was always precipitated in a very loose form on the cathode. This must be dissolved carefully in the nitric acid by heating the solution before it is made ammoniacal for the deposition of the silver.

Experiments.—The solutions contained 10 c.c. of concentrated nitric acid during the deposition of the lead. In No. 2, 5 c.c. more were added after the lead had been removed, to ensure the solution of all the silver, then the electrolyte was made strongly ammoniacal and the silver deposited. The lead peroxide was precipitated on the outer, the silver, after the removal of the latter, on the inner electrode :

No.	Taken.	Found.	Amps.	Volts anode-cathode.	Temp.	Time in minutes.
1.	0·2848 Pb	0·2857 Pb	3—4	1·6	boiling	10
	0·2694 Ag	—	—	—	—	—
2.	0·2848 Pb	0·2854 Pb	3	1·7	boiling	10
	0·2694 Ag	0·2693 Ag	3	—	,,	—

When lead peroxide is deposited from solutions containing salts of bismuth, it is known always to contain some of this metal and a purely electrolytical method of separation of lead from bismuth has hitherto not been available. It was expected that a separation might be effected by regulating the potential of the anode. This, however, proved not to be the case. In an experiment carried out with 0·15 gram of lead per 85 c.c. it was found that all the peroxide could be deposited at an anode-potential of 1·10 volts, the initial current being 3 amperes.

When, however, about 0·4 gram of bismuth was added as nitrate to the same lead solution, the lead appeared to be held back by the bismuth, for, in order to obtain the same current, an anode potential of 1·30 volts had to be employed, and it was only when the bismuth was removed on the cathode that the potential of the anode could be reduced. It appears that the only explanation which may be given for this is that the lead combines with the bismuth in complex molecules (possibly also as complex ions) which require a higher anode potential for their oxidation than the molecules of pure lead nitrate. This matter is of considerable interest inasmuch as, so far as I am aware, we have hitherto had no evidence for the formation of complex molecules in solution between such substances as lead and bismuth nitrate.

The separation of bismuth from lead by graded potential of the cathode was then tried. In their *Analyse des Métaux par Electrolyse*, 1906, p. 90, Hollard and Bertiaux describe a method by which small quantities of bismuth may be separated from lead in forty-eight hours. The lead is made insoluble by converting it into the sulphate and adding alcohol. The bismuth is then deposited by the current. As has already been explained (p. 397), methods of this kind in which insoluble precipitates are suspended in the electrolyte are not suitable for the rotating electrodes used in the present investigation.

Attempts were made to separate bismuth from lead in tartrate and in nitrate solutions. The former failed as the bismuth always contained lead. The latter, however, were successful. Either glucose or tartaric acid was added to the solution to prevent the formation of lead peroxide on the anode. In the former case the deposit of bismuth was somewhat loose. This becomes especially noticeable when bismuth and copper are precipitated together (see p. 408). After the bismuth has been removed the lead is deposited from the same solution, but it was found necessary to weigh the anode as well as the cathode, as small quantities of lead peroxide were usually formed. Although very crystalline, the metal adhered sufficiently to allow it to be washed. When tartaric acid was employed as a reducing agent the deposit of bismuth was quite firm, but it was found necessary to make the solution ammoniacal for the deposition of the lead.

Experiments.—In experiments 1, 2, 3, the electrolyte contained about 2 c.c. of concentrated nitric acid and 15 grams of glucose, the volume being 85 c.c. during the precipitation of the bismuth; in experiment 4, 2 c.c. of concentrated nitric acid and 20 grams of glucose were employed. Owing to the large quantity of lead present in the latter experiment the metal was deposited in a form too loose for accurate determination (error 5 milligrams). The numbers in brackets represent the amount of lead found as peroxide on the anode. In experiment 5 the solution contained 1·6 c.c. of concentrated nitric acid and 15 grams of tartaric acid; in experiment 6, one c.c. of concentrated nitric acid and 20 grams of tartaric acid. In the latter case the solution was made strongly alkaline with 20 c.c. of concentrated ammonium hydroxide before the deposition of the lead. The second number represents the lead determined as peroxide by dissolving in nitric acid and reprecipitating:

No.	Taken.	Found.	Amps.	Volts anode-cathode.*	Volts auxiliary.	Temp.*	Time in minutes.
1.	0·3886 Bi	0·3900 Bi	3—0·2	—	0·42—0·55	60—70°	9
	0·3560 Pb	0·3552 Pb (3·8 mg.)	3	—	0·90—0·95	—	11
2.	0·3886 Bi	0·3903 Bi	3—0·2	1·8	0·43—0·55	60—70	11
	0·3560 Pb	0·3557 Pb	3	2·4	0·85—0·90	60—80	10
3.	0·3886 Bi	0·3892 Bi	3·5—0·2	1·9	0·42—0·55	70—80	11
	0·2856 Pb	0·2856 Pb (4·9 mg.)	3	2·2—2·6	—	65	15
4.	0·3109 Bi	0·3129 Bi	3—0·2	—	0·43—0·55	70	8
	0·7120 Pb	0·7076 Pb (23·1 mg.)	—	—	—	—	—
5.	0·3109 Bi	0·3123 Bi	3·5—0·2	—	0·45—0·55	75	8
	0·2848 Pb	—	—	—	—	—	—
6.	0·1554 Bi	0·1555 Bi	1·6—0·2	—	0·43—0·55	55—80	12
	0·2848 Pb	0·2853 Pb 0·2841 Pb	2	1·4	1·04—1·50	boiling	10

* Rough values.

Cadmium and its Separation from all the preceding Metals.—The estimation of cadmium on a rotating cathode has been examined in considerable detail by Flora (*loc. cit.*). For the purposes of the present investigation, it was thought specially desirable to be able to deposit the metal from nitrate solutions, and a considerable number of experiments were carried out for this purpose.

The only solutions in which the potential of the electrode could be pushed high enough for the complete deposition of the metal were neutral and alkaline ones, as the potential is kept too low in acid solutions by the reduction of the nitric acid. In order to obtain adherent deposits, the electrolyte must be strongly alkaline; the precipitates obtained from ammoniacal solutions are loose and useless. Experiments are quoted below for cyanide solutions, but the electrolyte principally used in the present investigation contained sodium tartrate. This liquid must be employed cold, as an insoluble, white precipitate from which it is very difficult to deposit the metal separates from hot solutions. When the current has passed for some time the solution appears to undergo a change, possibly in consequence of the formation of oxalic acid by oxidation of the tartrate, which either necessitates a very high potential of the cathode for the complete precipitation of the metal or makes it altogether impossible.

The method adopted to overcome this difficulty was to make the solution slightly ammoniacal at the end of the experiment, either by adding ammonium sulphate and boiling for some time until most of the ammonia had disappeared, or by first making the solution faintly acid and then faintly ammoniacal. Although the last traces of the metal separate in a slightly powdery state under these conditions, they adhere sufficiently to allow the deposit to be washed. As will be seen from the numbers given below, there is then a decided tendency for the results to be high, so that it may be desirable to redeposit the metal.

The great variability of the deposition-potential of metals in neutral and alkaline solutions containing organic substances (including cyanides) was a phenomenon generally observed. It is due to the changes which these substances undergo at the anode. In consequence these solutions are in general much less suited for separations by graded potential than acid ones, and the results obtained from them are not so trustworthy as the beautiful appearance of the deposits would lead one to expect.

Acetate solutions containing free acetic acid were employed for the separation of cadmium from zinc. The deposits are somewhat loose, and in consequence the results not trustworthy for very large quantities of metal. The largest amount accurately deposited was 0·15 gram. As has already been explained, nitrates must not be present in these acid electrolytes. All the depositions were carried out with a limited potential of the cathode.

Experiments.—In Nos. 1 and 2, cadmium was deposited on the cathode from a tartrate solution, weighed, then dissolved in an acid solution containing 2 c.c. of concentrated sulphuric acid, then 8 grams of sodium tartrate and 5 grams of sodium hydroxide were added, and the solution electrolysed until no cadmium could be detected by hydrogen sulphide. The subsequent experiments were either carried out with a solution made up from pure cadmium sulphate (Kahlbaum), and analysed according to the method proved correct by experiments 1 and 2, or with a solution prepared by dissolving a weighed quantity of electrolytically prepared cadmium in sulphuric acid. In No. 3, 2 c.c. of concentrated sulphuric acid and $3\frac{1}{3}$ grams of sodium hydroxide were added to the electrolyte, which was then acidified with $1\frac{1}{4}$ c.c. of glacial acetic acid. The quantities taken in No. 4 were 2 c.c. of concentrated sulphuric acid, $3\frac{1}{3}$ grams of sodium hydroxide, and 2 c.c. of acetic acid. In No. 5, 3 c.c. of concentrated sulphuric acid and 10 c.c. of concentrated ammonium hydroxide were added, and the solution was then acidified with $4\frac{1}{2}$ c.c. of glacial acetic acid:

No.	Cd taken.	Cd found.	Amps.	Volts anode-cathode.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·3980	0·3983	5—0·3	2·9—2·3	1·45—1·60	cold	10
2.	0·4892	0·4890	5—0·3	—	1·45—1·60	,,	15
3.	0·1554	0·1554	4—1	2·6—2	1·12—1·20	80°	13
4.	0·1554	0·1547	3—1	—	1·12—1·20	70	—
5.	0·0777	0·770	2—0·4	—	1·15—1·20	45	8

Separation from the preceding Metals.—Cadmium is only deposited from acid solutions at a potential of the $2/N$ sulphuric acid electrode of more than 1 volt. Even when no auxiliary electrode is employed there is therefore no difficulty in hindering its precipitation by the addition of small quantities of nitric or large quantities of sulphuric acid. Of the metals dealt with in the present paper, the one nearest it in the electropotential series is lead; a separation from this metal therefore involves the separation from the rest. Results are also given below for bismuth. This was deposited either from a nitrate solution containing free nitric and tartaric acid or from a tartrate solution containing only free tartaric acid. In the former case, the potential of the auxiliary electrode was taken to 0·55 volt, in the latter to 0·70 volt. In both cases the current falls to about 0·2 volt when all the metal has been deposited. This does, however, not take place in the nitrate solutions if a reducing agent such as tartaric acid is not added.

For the separation of lead from cadmium a nitric acid solution was used containing glucose, and the potential of the auxiliary electrode was taken to 0·90 volt. The temperature should not be much below 60° and not above 80°. The current in this case does not fall to almost zero, but the course of the analysis may be readily followed if the approximate absence of lead is tested for by means of sulphuric acid. As a small amount of peroxide is generally deposited on the anode, the latter must be weighed before and after the experiment.

Experiments.—In No. 1, the solution contained $2\frac{1}{2}$ c.c. of concentrated nitric acid and 18 grams of tartaric acid for the determination of the bismuth; before the determination of the cadmium it was made alkaline with 17 grams of sodium hydroxide. In No. 2, the quantities were $2\frac{1}{2}$ c.c. of concentrated nitric acid and 12 grams of tartaric acid. In No. 3, the solution for the deposition of bismuth was identical with No. 2; for the determination of the cadmium it was made strongly alkaline with $3\frac{1}{3}$ grams of sodium hydroxide, the deposition of the latter metal was carried on for ten minutes in the cold, then 15 grams of ammonium sulphate were added, and the electrolysis continued in a boiling solution for nine minutes. In experiment 4, the solutions were identical with No. 3, but during the deposition of the cadmium the electrolyte was heated; in consequence it became turbid, 15 grams of ammonium sulphate were then added, but a considerable time was required to make the solution clear again.

In experiment 5, the solution contained 0·25 c.c. of concentrated nitric acid and 15 grams of glucose for the determination of the lead; before the estimation of the cadmium it was made alkaline with $3\frac{1}{3}$ grams of sodium hydroxide, and two-thirds of a gram of potassium cyanide was added.

In experiment 6, the solution for the determination of the lead was the same as in No. 5; for the estimation of the cadmium 8 grams of sodium tartrate and $3\frac{1}{2}$ grams of sodium hydroxide were added, the electrolysis was carried on for 30 minutes in the cold, and then continued at boiling temperature. The numbers in brackets give the weight of lead found as peroxide on the anode (dried only by alcohol and ether). In all these experiments the cadmium was deposited until constant in weight.

No.	Taken.	Found.	Amps.	Volts anode-cathode.*	Volts auxiliary.	Temp.*	Time in minutes.
1.	0·3886 Bi	0·3878 Bi	3—0·2	1·7	0·43—0·55	80°	10
	0·3887 Cd	0·3880 Cd	2	2·7	—	cold	18
2.	0·3886 Bi	0·3886 Bi	3—0·2	—	0·60—0·70	boiling	7
	0·3887 Cd	—	—	—	—	—	—
3.	0·3886 Bi	0·3867 Bi	3—0·2	1·4	0·60—0·70	boiling	7
	0·3887 Cd	0·3905 Cd	3	3	—	cold, then boiling	19
4.	0·3886 Bi	0·3884 Bi	3—0·2	1·6	0·60—0·75	80°	10
	0·3887 Cd	0·3862	—	—	—	—	—
5.	0·2848 Pb	0·2841 Pb (0·5 mg.)	3—1·8	2·7	0·80—0·90	70°	12
	0·3752 Cd	0·3771 Cd	3	3·8—4·5	1·40—2·00	cold	55
6.	0·2848 Pb	0·2846 Pb (1·0 mg.)	3—1·2	—	0·83—0·90	80	10
	0·3752 Cd	0·3787 Cd	3	3·5	—	cold, then boiling	55

* Rough values.

Zinc and its Separation from all the Preceding Metals, and the Electrolytic Destruction of Nitric Acid in Solution.

It appears that the potential at which zinc is deposited from all its solutions is too high to allow it to be quantitatively estimated in the presence of nitrates. When the solution contains nitric acid, the latter must therefore be removed, before the precipitation of the zinc, either by evaporation with sulphuric acid or by reduction to ammonia. The former process is somewhat lengthy, and besides would be quite unsuitable in the presence of considerable quantities of organic substances such as glucose or tartaric acid. A series of experiments was therefore carried out for the purpose of determining the most suitable conditions for the rapid electrolytic reduction of nitric acid to ammonia.

It was shown by Luckow (*Zeitsch. anal. Chem.*, 1880, **19**, 11) that the presence of copper on the cathode catalytically causes this reduction to take place when an electric current is passed through a solution containing nitric and sulphuric acids, and since that time several investigations have been carried out, mainly with the object of employing this reaction for the estimation of nitric acid (see Vortmann, *Ber.*, 1890, **23**, 2798); Ulsch (*Zeitsch. Elektrochem.*, 1897, **3**, 546); Ingham (*J. Amer. Chem. Soc.*, 1904, **26**, 1251).

The method chosen in the present investigation consisted in depositing about 0·3 gram of spongy copper on the cathode. A sulphuric acid solution was employed for this purpose containing a large quantity of glucose, and the copper was deposited by a strong current in the cold, the stirrer moving slowly. This operation could be effected either in the electrolyte containing the nitric acid or in a separate solution. The reduction of the nitric acid was effected slightly below the boiling point of the solution by a strong current, the stirrer moving slowly. It is possible to follow the process by means of the auxiliary electrode, the potential of which rises from about 0·5 to 0·8 or 0·9 volt as the nitric acid is destroyed. The disappearance of the latter may be ascertained by the diphenylamine test.

Example.—Spongy copper was deposited from 250 c.c. of a solution containing 0·3 gram of copper as sulphate, 1½ c.c. of concentrated sulphuric acid and 15 grams of glucose, by a current of 10 amperes in three minutes.

The reduction of 1 c.c. of concentrated nitric acid in 100 c.c. of water containing 2 c.c. of concentrated sulphuric acid took place by means of the electrode prepared thus in twenty-three minutes slightly below the boiling point of the solution with a current of 10 amperes. During this process the potential of the auxiliary electrode rose from 0·52 to 0·80 volt. The stirrer was moving slowly.

Zinc.—For the determination of zinc, Exner (*loc. cit.*) recommended acetate and sodium zincate solutions. The only electrolyte employed in the present investigation was an acetate solution containing a small amount of free acetic acid. Alkali sulphates were always added, as these may be considered to be present in all practical cases. It was found difficult to deposit the last traces of zinc at temperatures much above 30°. As the electrolyte is usually heated above this temperature in consequence of the passage of the current, the beaker was in some of the experiments placed in a large dish containing cold water. The results show a slight tendency to be high.

Experiments.—A weighed quantity of purest zinc was dissolved in sulphuric acid, the slight residue filtered off, weighed, and found almost negligible; the solution was made up to a known volume and measured quantities taken.

In each experiment sulphuric acid was first added to the solution ; it was then made strongly alkaline with either sodium- or ammonium-hydroxide and then acidified with acetic acid. In a few cases ammonium acetate was also added. The quantities taken are given in the following table. In the table of results, the second number under zinc found represents the value obtained on depositing the metal to constant weight. For all these experiments the cathode was plated with copper :

No.	H_2SO_4 in c.c.	NaOH in grams.	Concentrated $NH_4 \cdot OH$ in c.c.	Glacial HAc in c.c.	NH_4Ac in grams.
1.	$1\frac{1}{2}$	$3\frac{1}{3}$	—	$1\frac{1}{2}$	—
2.	$1\frac{1}{4}$	$6\frac{2}{3}$	—	9	—
3.	3	$5\frac{1}{2}$	—	$1\frac{1}{4}$	—
4.	$1\frac{1}{4}$	—	10	8	—
5.	$1\frac{1}{4}$	—	10	8	—
6.	$1\frac{1}{4}$	—	$3\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$
7.	$1\frac{1}{4}$	—	$4\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$

No.	Zn taken.	Zn found.	Amps.	Volts anode–cathode.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·6175	0·6168	3	4—4·5	—	cold	30
2.	0·4943	0·4957	3	3·8—4	1·45—1·70	,,	18
3.	0·2529	0·2540	3—4	3·6—4·2	1·45—1·50	,,	13
4.	0·4943	0·4944 0·4957	3	3·8—4·3	1·50—1·55	,,	20 + 10
5.	0·4943	0·4946 0·4953	3	3·8—4·3	—	,,	20 + 10
6.	0·4943	0·4944	3	—	—	,,	30
7.	0·4943	0·4938 0·4945	3—4	3·6—4·2	—	,,	20 + 10

Separation from the preceding Metals.—As is known, there is no difficulty in separating zinc from the majority of the preceding metals in consequence of the high potential required for its deposition. Cadmium being the metal preceding it in the electropotential series, a separation from this metal in acid solution involves the separation from all the others. It was stated by Freudenberg (*loc. cit.*) that a separation of cadmium from zinc could be effected in alkaline cyanide solutions, but for the reasons stated above (p. 401), it seems doubtful whether trust can be placed on a method of this kind.

Several successful experiments were carried out in which cadmium was separated from zinc in a weak acetic acid solution at a potential of the auxiliary electrode limited to 1·20 volts. Attention should, however, be drawn here to two experiments in which the cadmium contained some zinc, and I have not yet succeeded in explaining them. The experiments were Nos. 4 and 5 of p. 400 in the paragraph on the separation of seven metals from one solution. The conditions were a low temperature (about 15—20°) and a slightly rough cathode as a result of dissolving the combined metals cadmium and zinc immediately before the deposition of the cadmium, possibly also as a result of the presence of a trace of spongy copper. This led to a considerable evolution of hydrogen at the potential at which the cadmium was deposited.

Our present knowledge will, so far as I can see, not afford an explanation, but the following interpretation may be put forward tentatively as the result of a preliminary experiment. If hydrogen is liberated simultaneously with zinc, the latter may be deposited, especially at low temperatures, at a much lower potential than that at which it is in equilibrium with its solutions. The metal is probably deposited primarily as a hydride at a potential intermediate between the equilibrium potentials of hydrogen and zinc. In the two experiments referred to, the electrode with the cadmium was replaced in the solution from which the latter had been deposited, so that the greater part of the metal passed into solution again. It was then redeposited at about 30°, giving the correct result quoted on p. 410.

Experiments.—The following reagents were added to the electrolyte. In Nos. 1 and 2, 2 c.c. of concentrated sulphuric acid, 3⅓ grams of sodium hydroxide, and 1 c.c. of glacial acetic acid; in Nos. 3 and 4, 2 c.c. of concentrated sulphuric acid, 4 grams of sodium hydroxide, 1 gram of ammonium acetate, and 1½ c.c. of glacial acetic acid:

No.	Taken.	Found.	Amps.	Volts anode–cathode.*	Volts auxiliary.	Temp.*	Time in minutes.
1.	0·0777 Cd	0·0778 Cd	2—0·8	2·7	1·15—1·20	cold	11
	0·4943 Zn	0·4938 Zn	4	4·5	—	,,	20
2.	0·0777 Cd	0·0770 Cd	2·4—1	3—2·6	1·15—1·20	30°	12
	0·4943 Zn	0·4958 Zn	3	4·3	—	—	25
3.	0·0777 Cd	0·0770 Cd	2—0·5	—	1·15—1·20	35	12
	0·2514 Zn	—	—	—	—	—	—
4.	0·0777 Cd	0·0775 Cd	1·2—0·3	3—2·6	1·15—1·20	37	12
	0·2514 Zn	—	—	—	—	—	—

* Rough values.

The Rapid Separation of more than Two Metals from One Solution.

The difficulties met with in the rapid separation of a large number of metals from one solution are twofold. Firstly, the solution may become so much diluted by the wash-waters that it may be necessary to concentrate it by evaporation, involving loss of time. Secondly, a more serious difficulty is met with when large quantities of organic substances are present which by their oxidation may lead to the formation of compounds which either by chemical combination or owing to their viscid nature may retard the deposition of the other metals. As a rule, it will therefore be found best to precipitate more than one metal at a time and redissolve and separate the mixture.

If possible, the use of organic substances should be avoided in those solutions from which more than two metals are to be precipitated. The records of the following experiments will illustrate these remarks.

a. *Three Metals in One Solution. Lead, Cadmium, and Zinc.*

In experiment 1 a solution of the nitrates was taken containing about 0·2 c.c. of free nitric acid, 15 grams of glucose were added and the lead was precipitated as metal on the cathode (p. 402). The potential of the auxiliary electrode was taken to 0·90 volt, and the duration of the experiment was seven minutes. The number in brackets was the amount found on the anode as peroxide. The nitric acid was then destroyed (p. 404) in twenty-seven minutes, 2 c.c. of concentrated sulphuric acid and 0·3 gram of copper as sulphate having been added to the electrolyte. After the reduction of the nitric acid, the electrode was allowed to stand for several minutes in the acid liquid to allow any cadmium which might have been precipitated on the copper to pass into solution. The liquid was then filtered from particles of the spongy copper which had fallen off the electrode. Traces of copper which had gone into solution were deposited on the cathode in five minutes at a potential of the auxiliary electrode of 0·40 to 0·60 volt. The free sulphuric acid was then replaced by acetic acid by the addition of $6\frac{2}{3}$ grams of sodium hydroxide and 2 c.c. of glacial acetic acid, and the cadmium and zinc precipitated together from the cooled liquid. The combined precipitate was then dissolved in a solution to which 1·2 c.c. of concentrated sulphuric acid was gradually added, and the cadmium deposited after the addition of $3\frac{1}{3}$ grams of sodium hydroxide and $3\frac{1}{2}$ c.c. of glacial acetic acid. The potential of the auxiliary electrode was taken to 1·20 volts, and the duration of the experiment was twelve minutes. From the remaining liquid the zinc was deposited by 3 amperes in half an hour. Experiment 2 is an earlier determination in which all the metals were deposited in succession from the same liquid :

	Pb.	Cd.	Zn.
Taken	0·1424	0·938	0·2574
Found, No. 1 ...	0·1416 (1·0 mg.)	0·948	0·2581
Found, No. 2 ...	0·1424 (1·7 mg.)	0·936	0·2605

b. *Four Metals in One Solution. Copper, Bismuth, Lead, and Cadmium.*

Experiment 3.—A solution of the nitrates was taken containing nearly 1 c.c. of free nitric acid. The solution was first electrolysed at 60°, the potential of the auxiliary electrode being taken from

0·35—0·55 volt. Practically the whole of the lead and part of the bismuth were deposited on the anode, and all the copper and the rest of the bismuth on the cathode. As the current did not fall to zero, a much longer time than was probably necessary for the deposition, namely, twenty minutes, was employed. The cathode was then weighed, and the bismuth in the deposit determined according to the cyanide-tartrate method (p. 396), the electrolysis being continued for nineteen minutes. This gave the weight of the copper by difference. Before this determination the deposit on the anode had been completely dissolved in a solution containing 2 c.c. of concentrated nitric acid and 20 grams of tartaric acid at slightly below the boiling point, and from this liquid the remaining bismuth was deposited on the first portion according to experiments 5 and 6, p. 400. The lead was next deposited as metal (p. 400, No. 6), and the result checked by dissolving it in nitric acid and depositing on the anode (second figure given).

In the liquid remaining from the first operation, the cadmium was determined according to experiment 6, p. 403. It was then dissolved in nitric acid and the trace of lead present deposited on the anode. The correction found for lead amounted to 0·8 milligram :

	Cu.	Bi.	Pb.	Cd.
Taken	0·3682	0·1554	0·1424	0·0938
Found	0·3702	0·1534	0·1438 0·1427	0·0945

c. *Seven Metals in one Solution. Silver, Mercury, Copper, Bismuth, Lead, Cadmium, and Zinc.*

Experiment 4.—In this experiment, much difficulty was experienced from the causes outlined above. It was attempted to prevent the precipitation of the lead on the anode by the addition of 16 grams of glucose at the beginning of the experiment. The silver and mercury were first precipitated together and then separated from each other as described on p. 390, the potential of the auxiliary electrode being taken to 0·15 volt, and the mercury employed for plating the cathode amounting to about 2½ grams. From the remaining liquid, the copper and bismuth were precipitated together and then separated as described on p. 396. Owing to the presence of the glucose, both the first deposits were somewhat loose. In consequence, small particles of metal were seen in the wash-waters. These were filtered off, dissolved in nitric acid added to the original solutions, and corrections made by precipitating the traces left in the same way as the first two deposits. The corrections were 1·6 and 3·6 milligrams. After this, the solution had become so dilute that it was thought advisable to concentrate it by partial evaporation. It had, however, become so much charged with decomposition products of the sugar that the lead was not completely deposited at its proper potential. The nitric acid in the solution was reduced electrolytically as described on p. 404, and all the remaining metals were precipitated as completely as possible. The deposit thus obtained was dissolved in sulphuric acid and the cadmium separated from the zinc (see p. 405). The results for cadmium marked with an asterisk in experiments 4 and 5 are the second obtained, the first having been nearly a centigram too high in both cases. This was probably a result of the rough surface of the electrode left after the solution of the zinc combined with the low temperature employed. All the zinc was not precipitated, the presence of the large amount of decomposition products of the sugar having evidently made its complete deposition impossible. The amount obtained is the first number on the table. It was then attempted to obtain the remainder by adding ammonia and ammonium sulphide to the solution and allowing it to stand for several days at about 40°. The small amount of sulphide which separated out was collected and the zinc determined electrolytically, the weight being added to the first result (second number given). Even with this correction the result is low. The copper employed for the electrolytic reduction of the nitric acid and the cadmium were both examined electrolytically for lead. In the former, 2·3 milligrams were found, and this number was added to the result originally obtained, giving the number quoted.

Experiment 5.—The amount of free concentrated nitric acid present in the solution was again slightly less than 1 c.c. No organic substance was added to the electrolyte, but the separation was carried out in a manner similar to experiment 3 on p. 407. In the first deposition, the potential of the auxiliary electrode was taken to 0·15 volt in a boiling solution. This gave the silver and mercury on the cathode and hardly any lead on the anode. The cathode was plated with mercury for this deposition as in the previous experiment. The second deposition, in which the potential of the auxiliary electrode was taken to 0·55 volt, gave nearly all the lead and part of the bismuth on the anode, all the copper and the rest of the bismuth on the cathode. These deposits were treated as in experiment 3. The nitric acid was reduced electrolytically, and the zinc and cadmium first deposited together and then separated as in the preceding experiment 4. The same difficulty was again met with. The traces of lead which did not separate at the anode in the second deposition were recovered electrolytically as peroxide from the cadmium.

Experiment 6.—This experiment was carried out as No. 5, but the roughening of the cathode immediately before the precipitation of the cadmium which arose out of the method of working in the preceding experiments was avoided. After the deposition of the copper, bismuth, and lead, the nitric acid was expelled by evaporating the electrolyte almost to dryness on the water-bath with 3 c.c. of concentrated sulphuric acid. In the residue, the cadmium and zinc were determined as described on p. 405. In experiments 5 and 6, the results for lead were checked by dissolving the metal and redepositing it as peroxide. Both numbers are quoted.

No difficulty was encountered in experiment 6. The times of deposition were: silver *plus* mercury, 10 minutes; silver, 8 minutes; lead and part of the bismuth on the anode, copper and the rest of the bismuth on the cathode, 15 minutes; separation of the bismuth from the combined deposits of copper and bismuth, 15 minutes; separation of the rest of the bismuth from the combined peroxides of lead and bismuth, 10 minutes; lead as metal, 7 minutes; as peroxide, 10 minutes; cadmium, 15 minutes; zinc, 15 minutes; examination of the cadmium for traces of lead, 5 minutes.

Results of Experiments 4, 5, *and* 6.

No.		Ag+Hg.	Ag.	Cu.	Bi.	Pb.	Cd.	Zn.
	Taken...	0·2244	0·1078	0·1841	0·1554	0·1424	0·0938	0·1287
4.	Found...	0·2231	0·1099	0·1861	0·1557	0·1401	0·0949 *	0·1175 0·1228
	Taken...	0·2244	0·1078	0·3682	0·1554	0·1424	0·0938	0·1287
5.	Found...	0·2247	—	0·3696	0·1552	0·1461 0·1429	0·0935 *	0·1289
6.	Found...	0·2249	0·1098	0·3682	0·1548	0·1455 0·1441	0·0935	0·1311

In conclusion, it should be again pointed out that the electrodes here described may be used without an auxiliary electrode in all the cases of separation by graded potential which give trustworthy results by the slow methods hitherto known. Owing to their small resistance, they allow a current to be employed, even under this condition, which is sufficient to permit the metals to be deposited in a small number of minutes.

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