ON THE RECIPROCAL REPLACEMENT OF THE METALS IN AQUEOUS SOLUTIONS.

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EXPERIMENTS, for the purpose of comparing the rates at which magnesium liberates hydrogen from various aqueous solutions, have recently been performed by Kahlenberg;[1] and at his suggestion, G. Fernekes[2] undertook to find out whether sodium and potassium would act in a similar manner towards aqueous solutions. On account of the violence of the reaction in their case, and because the metals are so easily oxidized, amalgams of sodium and potassium were used instead of the metals themselves.

Fernekes found that solutions of sodium, potassium, barium, and certain other chlorides, for example, are more slowly acted upon by sodium and potassium amalgams than is pure water. Furthermore, he found that the retardation of the rate of evolution of hydrogen by sodium or potassium amalgam is about the same for isotonic solutions of sodium chloride and potassium chloride. He did not think these results were in harmony with the ionic theory.

In his investigation, Fernekes, besides acting on sodium amalgam with solutions of sodium salts, also acted upon it with solutions of potassium salts, then with hydrochloric and nitric acids, and finally, with salts of ammonium, barium, calcium, and strontium. In this case, as has long been known, potassium, ammonium, barium, calcium and strontium are all capable of replacing sodium in sodium amalgam.

Fernekes also acted with potassium amalgam on solutions of sodium and potassium salts.

It has been shown in a former paper[3] that potassium is capable of replacing sodium in its amalgam from a solution of potassium *chloride*, as well as from a solution of potassium hydroxide or carbonate. This was not known before, and Kraut and Popp (see below) state in their article, that such is not the case. On the other hand, it has been shown in the same place that sodium is

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[1] This Journal, **25**, 380 (1903); *cf.* also Roberts and Brown: *Ibid.*, **25**, 801.

[2] *Jour. Phys. Chem.*, **7**, 611 (1903).

[3] Smith: *Ibid.*, **8**, 212 (1904).

also capable of replacing potassium in potassium amalgam,[1] it being only necessary to act on potassium amalgam with a concentrated solution of sodium chloride.

Taking these facts into consideration, which Fernekes did not do, his results can readily be interpreted by the ionic theory. This has been done by the author.[2]

The reciprocal replacement of potassium and sodium is very interesting. It has long been known that potassium is capable of replacing sodium in sodium amalgam;[3] and Berthelot and others after him have called this replacement an anomaly. They explained it as the necessary consequence of the greater loss of energy undergone by potassium than by sodium in the formation of their respective amalgams.[4] That potassium in its amalgam might also be replaceable by sodium does not appear to have entered their thoughts.

From the electrochemical series, in which potassium is more electropositive than sodium, it was to be expected that the replacement of potassium in its amalgam by sodium would take place more readily than the reverse; and in a former paper[5] I have shown that this really is the case.

I have also shown that potassium and barium, as well as sodium and barium, are reciprocally replaceable in their amalgams.[6]

In attempting to bring about the replacement of barium in its amalgam by potassium, a solution of potassium chloride was first employed; and with indifferent success. But by acting on the amalgam with a solution of potassium hydroxide, the desired replacement was readily accomplished. In this case the hydroxyl ions of the solution tend, by mass action, to prevent the entrance there of more hydroxyl ions. The barium is, therefore, prevented from acting on the water of the solution; and, in order for it to get out of the amalgam, it must replace potassium in the solution—*i. e.*, potassium must enter the amalgam. The solubility product of the barium hydroxide formed is very soon exceeded in the

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[1] The author has since found that this fact was discovered also, almost simultaneously, by W. Kettembeil, who prepared sodium amalgam from potassium amalgam by acting on the latter with a solution of sodium hydroxide. (*Cf. Jour. Chem. Soc.* [London], 1904, *Abstr. ii.*, 173).

[2] *Jour. Phys. Chem.*, **9**, 13-35 (1905).

[3] Kraut and Popp : *Ann. Chem.* (Liebig), **159**, 188 (1871).

[4] Frémy : "Encyclopédie Chimique," (1885), sub sodium, p. 17 ; W. Kerp : *Z. anorg. Chem.*, **17**, 296 (1898).

[5] *Jour. Phys. Chem.*, **9**, 22 (1905).

[6] *Ibid.*, **9**, 16-23.

strong potassium hydroxide solution, and it separates in solid form. This, of course, also favors the replacement of the barium in the amalgam by potassium, the concentration of the barium ions in the solution being kept at a minimum.[1]

In general, according to Nernst,[2] when one metal is immersed in the solution of a salt of another metal, the following relation must hold, in order for the second metal to be precipitated by the first :

$$\frac{RT}{n_1} ln \frac{P_1}{p_1} > \frac{RT}{n_2} ln \frac{P_2}{p_2},$$

or

$$\sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}};$$

where the index 1 refers to the first metal, 2 to the second metal, and where P_1 and P_2 are the electrolytic solution-pressures, p_1 and p_2 the osmotic pressures of the monovalent ions, and n_1 and n_2 the valencies of the metals in question.

From this it follows that the following conditions are favorable for the precipitation of the second metal :

(1) High osmotic pressure (*i. e.*, high concentration) of the ions of the second metal.

(2) Great electrostatic pull—*i. e.*, high solution pressure of the first metal, and low osmotic counter-pressure (or low concentration) of the ions of this metal.

It is conceivable that any two metals might be reciprocally replaceable, depending on the relative magnitudes of $\sqrt[n_1]{\frac{P_1}{p_1}}$ and $\sqrt[n_2]{\frac{P_2}{p_2}}$ under different conditions ; and at least one such pair of metals has been known for some time, *viz.*, mercury and silver.

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[1] In this connection, the following data may be of interest. (*Cf. Jour. Phys. Chem.*, 9, 16-20.)

Barium amalgam (38.14g) was treated for one hour at the ordinary temperature with 25 cc. of a saturated solution of potassium hydroxide. There was no visible evolution of hydrogen, and considerable barium hydroxide separated in solid form.

The resulting amalgam gave:

0.1589g $BaSO_4$ (= 0.09354g Ba)

and 0.4104g K_2PtCl_6 (= 0.06614g K: equivalent to 0.1161g Ba)

The mother-liquor gave :

0.2038g $BaSO_4$(= 0.11995g Ba).

i. e., 53.3 per cent. of the barium in the amalgam was replaced in one hour by potassium.

In an analogous experiment with 40 grams of the same amalgam and 50 cc. of saturated potassium chloride solution, only 0.0086g K_2PtCl_6 was obtained from the resulting amalgam.

[2] Nernst : *Theoret. Chem.*, 3, *Aufl.* 668 and 674.

It is a well-known fact that mercury is capable of precipitating silver from a solution of silver nitrate. On the other hand, perhaps it is not so well known, that mercury can be precipitated from a solution of mercurous nitrate by silver;[1] and this process does not proceed anything like as readily as the first.

The following has also been known for some time[2] :

"Fügt man zum Kupfer im Daniellelemente eine hinreichend concentrirte Cyankaliumlösung, so werden die Kupferionen so weitgehend addirt, dass die elektromotorische Kraft der Kombination ihr Zeichen wechselt, d. h. in einer solchen Kombination geht Kupfer in Lösung und reduzirt das Zink.—Eine Reihe weiterer solcher Beispiele findet man bei Hittorf;[3] der zuerst derartige Fälle eingehender untersucht hat."

But in this case,—and the same applies to the cases described by Hittorf,[4]—there is an electric current to be taken into consideration; and, although zinc is reduced by copper, it is not precipitated on the copper pole, but on the zinc pole of the cell. Moreover, in this case, the copper and the zinc pole are immersed in solutions consisting essentially of potassium copper cyanide and of zinc sulphate, respectively.

The question now presented itself, whether metallic copper is capable of directly precipitating zinc from a zinc solution. It has been answered in the affirmative.

Reciprocal Replacement of Zinc and Copper.—That zinc will precipitate copper, even from a very dilute solution of copper chloride, for example, is very well known. By keeping the concentration of copper ions in a solution sufficiently low, and at the same time providing for the presence there of a relatively high concentration of zinc ions, it has been found possible to precipitate zinc directly from the solution by means of metallic copper.[5] This replacement does not readily take place, however, because

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[1] Ogg : *Chem. Centralblatt*, 1897, ii, 11; 1898, ii, 1077.

[2] Nernst : *Loc. cit.*, 672.

[3] *Ber. chem. Ges.*, **26**, R., 128 (1893).

[4] Hittorf found that, in the combination

$$\rightarrow Ag \mid CNK, KNO_3, NO_3Ag \mid Ag,$$

a galvanic current is produced in the direction indicated by the arrow, when the poles are brought into contact by means of a wire. He also found that this current does not disappear if for the silver cathode, immersed in silver nitrate solution, a cathode of copper, cadmium, or lead, immersed in the solution of a salt of the metal in question, is substituted. The silver is here electropositive in regard to the metals named, and it is seen that their positions in the electrochemical series do not determine the direction of the current in this case.

[5] Cf. Smith : *Jour. Phys. Chem.*, **9**, 31 (1905).

in reality the concentration of the zinc ions in the solution is exceedingly low.

A piece of bright copper foil was allowed to stand in a solution of potassium zinc cyanide, made by dissolving freshly prepared zinc cyanide in as little of a concentrated solution of potassium cyanide as possible, and then adding a slight excess of this solution. For a long time the copper remained unaltered, but after a day a distinct, bright coating of zinc could be seen on the copper. After five days the coating, which was still very thin, was tested, and found to be metallic zinc.

The same deposit can be obtained , in the course of an hour, by heating the copper with the solution, in a water-bath.

Reciprocal Replacement of Cadmium and Copper.—When a piece of cadmium is immersed in a solution of copper chloride in water, a precipitate of copper immediately commences to form on the cadmium. The reverse replacement was brought about in the same manner as that of zinc.

To a concentrated solution of cadmium sulphate, in a test-tube, was added concentrated potassium cyanide solution, until the precipitate at first formed was completely redissolved. A freshly polished piece of copper foil was then dropped into the solution, and the whole heated for one-half hour in a water-bath. At the end of that time a bright coating of cadmium had been deposited on the foil.

Reciprocal Replacement of Iron and Mercury, etc.—Upon the addition of a solution of potassium ferricyanide to mercury there is an immediate action, which becomes still more apparent, if a little potassium hydroxide is also added. In either case a thin, stiff coating of silky, metallic luster forms on the surface of the mercury.

In the absence of potassium hydroxide, a precipitate similar to Prussian blue separates; in its presence ferric hydroxide is precipitated. This is probably a secondary product, since the first precipitate is decomposed by potassium hydroxide with the formation of potassium ferrocyanide and ferric hydroxide.

That mercury is soluble in potassium ferricyanide, both in the presence and absence of potassium hydroxide, was shown as follows :

I. A solution of 7 grams of potassium ferricyanide and 1.5 grams of potassium hydroxide in 150 cc. of water was added to 101 grams of mercury, in an Erlenmeyer flask, and the mixture allowed to stand at the ordinary temperature, with occasional shaking. After two and one-half hours the solution had changed from a clear yellow, to an opaque, orange color. This was due to the formation of colloidal ferric hydroxide, a part of which had begun to separate out, and remained in suspension. In all, the mixture stood for seventy-seven hours. At the end of that time four layers could be distinguished; *viz.*, liquid mercury, finely divided mercury, ferric hydroxide, and solution. On shaking, the red precipitate went into suspension, and could be collected on a filter. It dissolved in hydrochloric acid with a yellow color, and the solution gave a dark blue precipitate with potassium ferrocyanide.

At the end of the above period, the solution was filtered off; it was still slightly alkaline, and was of a faint yellow color. A drop of it gave a dark blue precipitate with ferric chloride. This solution, when heated on a water-bath, gave a further deposit of ferric hydroxide; and, in order to remove this, the solution was evaporated to dryness, taken up in water, and filtered. The filtrate was again evaporated to dryness; it left a yellow residue, which consisted mainly of potassium ferrocyanide. This was treated with concentrated sulphuric acid, and the mixture evaporated just to dryness. The residue consisted mainly of anhydrous ferric sulphate, which had been formed as follows:[1]

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = FeSO_4 + 2K_2SO_4 + 3(NH_4)_2SO_4 + 6CO; \text{ and } 2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O + SO_2.$$

This residue went in solution only on long-continued heating with water. The solution was strongly acidified with sulphuric acid, and hydrogen sulphide passed in. The mercuric sulphide formed weighed 2.15 grams. This precipitate was dissolved in aqua regia, and the solution gave a bright deposit of mercury on copper foil.

II. To 102 grams of mercury was added a solution of 3 grams of potassium ferricyanide in 100 cc. of water, and the mixture allowed to stand, with occasional shaking, in a stoppered flask, for four days at the ordinary temperature. The liquid was then filtered.

The precipitate consisted of a dark blue substance, similar to Prussian blue, which ran through the filter on washing. It was

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[1] Treadwell's "Analytische Chemie," 3 Aufl., p. 97; Roscoe and Schorlemmer, Vol. II, Pt. ii, (1891), p. 101.

decomposed by potassium hydroxide solution, with formation of ferric hydroxide and potassium ferrocyanide.

The filtrate was greenish yellow in color, and a drop of it gave with ferric chloride a dark blue precipitate. It was evaporated on a water-bath, and gave on heating a further precipitate, similar to the first. The filtrate on being evaporated to dryness left a residue resembling potassium ferrocyanide. It was treated with sulphuric acid, and the mixture evaporated just to dryness; the residue was heated over night with water on a water-bath. The resulting solution was treated with a little sulphuric acid, and then with hydrogen sulphide. The precipitate obtained was extracted with carbon bisulphide to remove the sulphur. Result: 0.2358 gram HgS.

The residue of mercury was examined for iron in both cases. It had every appearance of an amalgam, and must have contained iron, in small quantity. The finely divided particles were not magnetic; neither was the film on the surface of the mercury appreciably attracted by a magnet. After washing with sodium hydroxide, and then with water, the mercury was tested for iron. It was extracted with nitric acid, which immediately rendered the mercury mobile; the extract was evaporated to dryness, and the residue taken up in dilute hydrochloric acid. The mercury was removed with hydrogen sulphide, and the filtrate evaporated to dryness with the addition of a little nitric acid. Potassium ferrocyanide was then added.

In another test the mercury was expelled from a portion by heating it in a porcelain crucible. A trace of residue was left. This was treated with concentrated hydrochloric acid, and the mixture evaporated to dryness on a water-bath. Then a drop of potassium ferrocyanide was added.

In these tests only traces of iron were found, and once or twice not even that.

Since the mercury went in solution, even in the presence of potassium hydroxide, it must have been in the form of potassium mercuric cyanide.

From the foregoing the following reactions are probable:

(*a*) $4K_3Fe(CN)_6 + 6Hg = 6K_2Hg(CN)_4 + 4Fe$;[1]

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[1] This reaction appears to be reversible. Iron turnings, which had been freed from oil by ignition, and then from oxide by treatment with hydrochloric acid, were heated for three hours in a water-bath with a solution of 1.04 gram mercuric cyanide and 0.52 gram potassium cyanide in 20 cc. water. The reaction proceeded very slowly, but at the end of

(*b*) $3K_3Fe(CN)_6+4Fe=Fe_4(Fe(CN)_6)_3+9K$;
(*c*) $9K_3Fe(CN)_6+9K=9K_4Fe(CN)_6$;

and, in case potassium hydroxide was also added,

(*d*) $Fe_4(Fe(CN)_6)_3+12KOH=3K_4Fe(CN)_6+4Fe(OH)_3$.

The transitory separation of metallic iron is further borne out by the fact that metallic iron gives, with potassium ferricyanide solution, a precipitate similar to the one obtained above, and that it gives with the same solution, in the presence of potassium hydroxide, a reddish precipitate of ferric hydroxide.

Potassium amalgam reduces potassium ferricyanide to potassium ferrocyanide; and, if the ferricyanide solution is present in excess, it acts upon the mercury as soon as all the potassium has been removed.[1]

Reciprocal Replacement of Mercury and Silver.—As is well known, silver is readily precipitated from a solution of silver nitrate by mercury.

In this case the reverse replacement has been brought about by acting on silver with various salts of mercury. These experiments are of especial interest, in that they tend to strengthen conclusions already arrived at by the conductivity method and others, as to the slight degree of dissociation of certain salts of mercury in aqueous solution.

In the following experiments samples of silver purified in various ways were used, and all gave similar results. The metal used in the experiments here described, however, was prepared by precipitating the silver from an aqueous solution of silver nitrate by means of pure granulated zinc. The excess of zinc was removed by the addition of hydrochloric and sulphuric acids to the mixture of silver and zinc, and digesting for twenty-four hours on a

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this time the solution gave a greenish coloration with ferric chloride, to which a slight amount of hydrochloric acid had been added; and the metal upon being heated in a porcelain crucible with a bright copper lid, gave a slight deposit of mercury on the copper.

Potassium ferrocyanide has no perceptible action on mercury, either in the presence or absence of potassium hydroxide. This is readily explained by the fact that the ratio 1:2 does not hold for the potassium and cyanogen in this salt.

[1] Results in every way analogous to those obtained with mercury, were also obtained with silver. With copper, potassium ferricyanide solution alone gives a bright red deposit, which turns dark on exposure to the air. Treated with concentrated hydrochloric acid, this deposit leaves a faintly yellow residue. It is therefore not iron hydroxide.

In none of these cases have I succeeded in definitely confirming the presence of metallic iron in the reaction products. The smallest particles are not attracted by a magnet, although once or twice out of numerous trials fragments seemed to be slightly magnetic, while in the solution, but quickly lost this property, especially on being taken from the liquid. These exceptions are by no means convincing.

radiator.[1] The silver was washed by decantation, treated with ammonia and thoroughly washed again. It was then dried on a water-bath and finally ignited. Thus prepared it presented a spongy appearance.

The following experiments were performed:

(1) Five-tenths gram silver was heated for half an hour in a water-bath with 10 cc. of a solution of mercuric chloride, which at that temperature contained a slight excess of the solid salt. The metal was then thoroughly washed with hot water, dried, and finally heated in a porcelain crucible which was covered with a weighed piece of freshly polished copper foil. The crucible was held in a punctured asbestos plate and the copper lid was kept cool by placing upon it a 100 gram weight. The mercury expelled by the heat from the silver condensed on the copper foil, and the increase in weight of the latter gave the weight of mercury in the silver amalgam—in this case 0.15 gram.

(2) The same experiment was performed with 0.5 gram silver and 10 cc. of saturated mercuric cyanide solution. After having been heated for half an hour in a water-bath the metal was thoroughly washed with hot water and then tested as above. The deposit of mercury was unmistakable, but it weighed only 0.0010 gram.

(3) To 0.5 gram silver in a test-tube was added 3.3 grams potassium cyanide and 6.3 grams mercuric cyanide, and then 10 cc. water. Immediately on the addition of the water the silver turned dark, owing to the deposition of mercury on its surface. The test-tube was heated in the flame of a Bunsen burner until the salts were completely dissolved; it was then further heated in a water-bath. In all, the heating lasted half an hour. The resulting amalgam, which was semi-liquid, was treated as described under (1). The mercury deposited on the copper foil weighed 0.41 gram. This reaction is reversible, and will be found suitable for the study of an equilibrium, probably approachable from either side.

(4) An experiment was carried out with silver and mercuric nitrate, but the salt was hydrolyzed to such an extent that it was practically impossible to separate the porous silver from the yellow oxide which separated. The same experiment, carried out with a sample of silver which had been melted to a compact globule,

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[1] A sample of the zinc used in the precipitation of the silver was treated as above, and it dissolved without leaving a residue.

showed, however, that silver is capable of precipitating mercury from this salt also.

(5) Finally, 10 cc. of a cold, saturated mercurous nitrate solution, which had been kept over a mixture of the solid salt and metallic mercury, was heated as above for half an hour with 0.5 gram silver. The metal was then thoroughly washed, dried and tested as described under (1). A deposit of mercury was obtained which weighed 0.2487 gram.

The reactions may be represented as follows:

(1) $2Ag + HgCl_2 = 2AgCl + Hg.$[1]
(2) $2Ag + Hg(CN)_2 = 2AgCN + Hg.$
(3) $2Ag + K_2Hg(CN)_4 = 2KAg(CN)_2 + Hg.$
(4) $2Ag + Hg(NO_3)_2 = 2AgNO_3 + Hg.$
(5) $2Ag + Hg_2(NO_3)_2 = 2AgNO_3 + 2Hg.$

The last reaction has been found suitable for the study of an equilibrium, which, however, is approachable from one side only.[2]

As was to be expected, the largest amount of mercury was obtained from the double cyanide of mercury and potassium. The relative amounts of mercury obtained from mercuric chloride, mercuric cyanide and mercurous nitrate are somewhat surprising at first glance. In aqueous solution the cyanide is the least dissociated of the three, and yet the amount of mercury obtained from it was over a hundred times as small as that obtained from either of the other two. This can, however, be explained as follows:

The solution of mercurous nitrate had a strongly acid reaction in the cold; when heated it was probably still farther hydrolyzed. The presence of free nitric acid facilitated the solution of silver, and at least a part of that which went into solution was replaced by mercury.

In the case of mercuric chloride, double chlorides of silver and mercury were probably formed, *e. g.*, according to the following equation:

$$3HgCl_2 + 2Ag = 2AgHgCl_3 + Hg.$$

This is supported by the fact that silver chloride is markedly soluble in a solution of mercuric chloride in water.

According to C. Jones,[3] when finely powdered silver is treated

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[1] In this case some calomel was also formed; the resulting metal was darkened by ammonia.

[2] Ogg: *Loc. cit.*

[3] *Ber. chem. Ges.*, **27**, R. 781 (1894).

in the cold for several weeks with an excess of mercuric chloride a double salt is formed as follows:

$$HgCl_2 + Ag = HgAgCl_2.$$

He says that this salt is blackened by ammonia, and is decomposed by concentrated ammonium chloride solution, according to the following equation:

$$3HgAgCl_2 = Hg + Ag + 2AgCl + 2HgCl_2.$$

Reciprocal Replacement of Mercury and Platinum.—A solution of chlorplatinic acid when treated with mercury gives a precipitate of metallic platinum, which is not very soluble in the mercury.

The reverse replacement can be brought about by heating metallic platinum with a concentrated solution of potassium mercuric cyanide.

A strip of platinum foil which presented a total surface of about 1 sq. cm. was heated in a water-bath for five hours with an excess of concentrated potassium mercuric cyanide solution. The foil, which was much less bright than originally, was thoroughly washed, dried and then tested for mercury, as in the preceding experiments. A deposit of mercury weighing 0.0002 gram was obtained on the copper foil.

Reciprocal Replacement of Mercury and Gold.—When a solution of gold chloride is treated with mercury the gold is reduced and forms an amalgam with the excess of mercury.

If, on the other hand, metallic gold is heated with a solution of potassium mercuric cyanide, gold goes in solution and mercury is precipitated on the surface of the gold.

Thirty-three hundredths gram of porous gold, obtained by the ignition of gold amalgam at a bright red heat, was heated for half an hour on a water-bath with an excess of concentrated potassium mercuric cyanide solution. The amalgam was thoroughly washed with hot water and then analyzed. It gave a deposit of mercury which weighed 0.0065 gram.

Reciprocal Replacement of Silver and Gold.—A small piece of pure gold was dissolved in a little aqua regia and the solution evaporated to a thick syrup. This was taken up in a little water, and a piece of silver added. It was at once covered with a dark deposit. After a short time the silver was taken out and washed, first with water and then with ammonia. It was found to be covered with a bright, loosely adhering coating of metallic gold.

The reverse replacement was accomplished by heating a small piece of gold with an excess of a concentrated solution of potassium silver cyanide. After two hours' heating in a water-bath the gold was covered with a white deposit. This deposit was washed with water, then with ammonia, and again with water. It was then dissolved in nitric acid, and with this solution hydrochloric acid gave a precipitate which was soluble in ammonia and which returned on the addition of nitric acid to the ammoniacal solution.

SUMMARY.

An abbreviated electrochemical series of the metals reads as follows: +K, Na, Ba, Sr, Ca, Mg, Al, Zn, Cd, Fe, Co, Ni, Sn, Pb, Cu, Hg, Ag, Pt, Au —.

The author has shown the metals in the following pairs to be reciprocally replaceable in aqueous solution, the metal first named in each pair being under ordinary circumstances more readily replaceable by the second than the second by the first.

K–Na; K–Ba; Na–Ba; Zn–Cu; Cd–Cu; (Fe–Hg); (Fe–Ag); Hg–Ag; Hg–Pt; Hg–Au; Ag–Au.

It is the intention of the author to continue the study of reciprocal replacements, as well in the presence of mercury as in its absence.

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A NEW SYNTHESIS OF HYDRONITRIC ACID.

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Several methods for the preparation of hydronitric acid from inorganic hydrazine compounds have been described. Curtius[1] obtained a dilute solution of the acid by passing the gaseous reduction products of nitric acid through a solution of hydrazine hydrate. Angeli[2] prepared silver trinitride by adding a saturated solution of silver nitrite to a solution of hydrazine sulphate. Dennstedt and Göhlich[3] made use of the interaction of hydrazine sulphate and potassium nitrite. Sabanejeff and Dengin[4] heated

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[1] *Ber. chem. Ges.*, **26**, 1263 (1893).

[2] *Atti. d. Reale Accad.* (5), **2**, I, 569; *Centrbl.*, II, 559 (1893).

[3] *Chem. Ztg.*, **21**, 876 (1897); *Centrbl.*, II, 1093 (1897).

[4] *Ztschr. anorg. Chem.*, **20**, 21 (1899).