As no elements with atomic weights between those of gadolinium and erbium were available for this work, a dotted line is used in this portion of the curve.

Conclusions.

It will be noticed that, although sulfates of samarium, europium and gadolinium gave approximately the same results, the tendency to hydrolyze throughout the series increased with increase in atomic weight.

Meyer[1] includes yttrium in his series. This element has an atomic weight of 89 and can not fit the curve formed by the rare earths, so it has not been used in this work. Considering actual rare earths, no sharp division of the elements into two series, when comparing basicity with atomic weights, has been found.

The results of this investigation indicate that, in the purification of gadolinium from samarium by fractional precipitation with ammonium hydroxide, the samarium would be concentrated in the tail fractions and not, as found by Boisbaudran[2] and Benedicks,[2] in the head. Concerning this difference the authors have at present nothing further to offer.

DURHAM, N. H.

ELECTROSTENOLYSIS.[3]

BY HARRY N. HOLMES.

Received March, 4, 1914.

Historical.

Braun and Coehn, who have done most of the work in this subject, made their capillaries by heating thick glass tubes, closed at one end, and plunging them into cold water. The tubes were shivered into a number of fine cracks which were really capillary spaces. A platinum anode with a water solution of some salt was placed in this tube, which rested in a beaker containing more of the same solution and the platinum cathode. On passing through a direct current at 40 v. or more, preferably 110 v., a spongy deposit of metal or oxide was found in the cracks.

Coehn[4] explained this phenomenon on the assumption that, when two substances are brought into contact with each other, the one possessing the higher dielectric constant will become positively charged. Since water has a very high dielectric constant it must be positive to most insoluble substances. The layer of water in contact with the walls of a glass capillary is positive and, under the influence of an electric current of sufficient voltage, must be attracted to the cathode leaving the glass

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[1] *Loc. cit.*

[2] *Ibid.*

[3] By electrostenolysis is meant the deposition of a metal or its oxide in very fine capillaries when the solution filling these capillaries is electrolyzed. Frequently there is an evolution of gas from the deposit.

[4] *Z. Elektrochem.*, 4, 501 (1898); *Z. physik. Chem.*, 25, 651 (1898).

wall of the capillary negatively charged. This negative charge increases to a point where it is great enough to discharge positive ions present, causing a deposit of metal or oxide in the capillary. Coehn believed that the deposit must always be slight because of the relatively heavy charge on the ions and small charge on the capillary wall. In most cases any minute deposit that may form can not increase to an appreciable amount because it takes part in conduction of the current, one end becoming an anode and losing as fast as the cathode end gains. Yet there are cases where this initial deposit increases to visible size. According to Coehn such cases are:

1. When the deposited metal is not oxidized at the anode as, for example, the platinum salts.

2. When an insoluble compound is formed at the anode, especially the peroxides.

3. When, in the case of salts in the lower state of oxidation, the negative ion can react with the solution with the formation of a higher oxidized salt; as in the case of a cuprous chloride solution. Here the chlorine liberated oxidizes the salt to cupric chloride.

4. Coehn[1] developed a qualitative test for cobalt in the presence of nickel salts and also a tedious quantitative separation of the two metals based on his observation that cobalt salts showed stenolysis, while nickel salts did not.

Richards and Lacy[2] proved that the complication of electrostenolysis does not affect the weight of the true cathode deposit or the exact application of Faraday's law.

Braun[3] obtained the following results:

Stenolysis with water solutions of
$Co(NO_3)_2$
$Pb(NO_3)_2$
$Pb(Ac)_2$
H_2PtCl_6
$HAuCl_4$
$Pd(NO_3)_2$
$Th(SO_4)_2$
$AgNO_3$
Ag_2SO_4
$AgAc$
$FeSO_4$
Na_2PtCl_6
Cu_2Cl_2

No stenolysis with salts of
Ni
Zn
Bi
Cu (except Cu_2Cl_2)
$KAg(CN)_2$
$FeCl_2$

The effective capillary surfaces in tubes prepared by Braun's method are very limited, offering great resistance to the passage of the current and yielding smaller deposits than are desirable. Furthermore, it is not

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[1] *Z. anorg. Chem.*, **33**, 9 (1903).

[2] THIS JOURNAL, **27**, 232 (1905).

[3] *Wied. Ann.*, **42**, 450 (1891); **44**, 473 (1891).

easy to examine the deposits chemically and the preparation of the tubes is tedious. In all cases the walls of the capillaries are glass. To devise more effective and convenient methods for studying this highly interesting phenomenon this work was undertaken.

Experimental.

Braun's method of preparing cracked glass tubes was duplicated, though at first only a small percentage of the tubes prepared were of any service whatever. On plunging the hot glass into cold water the tubes frequently broke into pieces, or the cracks were so wide as to leak rapidly or were mere surface fractures.

Repeated trials proved that soft glass tubing 2–3 mm. thick was most suitable. The closed end should not have too thick a mass of glass and, in general, it is safer to heat at a little distance from the closed end. The temperature requisite can only be determined by experiment. The glass must be just hot enough to shiver it into a network of fine cracks on quenching in water, but not hot enough to cause the tube to fall into pieces. A little practice enables one to prepare tubes with a beautiful lace-like surface and with capillaries so narrow that the tube will not leak more than a drop in an hour.

Using these capillary walls to separate anode and cathode, nearly all of Braun's experiments were readily duplicated. Solutions of cobalt chloride and cobalt nitrate quickly yielded black deposits with a direct current of 110 v. The cobalt deposit was fairly compact and formed in the crack, but the lead deposit was very spongy and appeared on the edge of the cracks nearest the anode. Solutions of chloroplatinic acid yielded most spectacular results, as the deposit spread from one crack to another forming a platinum mirror over the surface of the glass. Deposits of other metals were less striking, frequently extremely minute. Gassing from the cracks was common.

It was evident that an increase in the number of capillaries would give promise of increased deposits and with this in view glass tubes, U-shaped, were packed with various finely powdered insoluble substances and filled with water solutions of various salts to be tested by electrolysis. Naturally, glass powder was tried first and then precipitated and ignited silica. These were followed by flowers of sulfur, arsenic trisulfide, calcium fluoride, aluminium trioxide, lead sulfate, asbestos, shellac, kaolin, chromic chloride (violet) and starch paste. Of this list, powdered glass, sulfur and silica proved to be the best. In fact, no deposit at all could be secured in calcium fluoride, aluminium trioxide, lead sulfate, kaolin, starch paste and arsenic trisulfide. Possibly longer running may produce deposits with some of these powders.

With glass powders, the nature of the charge developed in contact with solutions is the same as with capillary cracks in glass tubes, but the surface exposed is enormously greater. Glass powder in water is sufficiently alkaline to precipitate many metallic hydroxides.

Sulfur possesses the advantage of a color that contrasts well with most stenolytic deposits and it can be secured in a finely divided form. Solutions diffuse through it so slowly that soaking for some hours is advisable before attempting electrolysis.

Silica, in the precipitated and ignited form, affords very fine capillary spaces and is free from the alkalinity of glass powder. Its white color is a distinct advantage.

To prepare the porous membranes, a soft glass tube about 1 cm. inner diameter was bent into a U about 8 cm. high. This was then packed with the proper dry powder for a length of about 5 cm. and the membrane held in place by two compact plugs of washed asbestos about 1 cm. deep. Without these asbestos plugs some light powders spread through the solutions. Finally the tube was filled with the solutions to be examined and platinum electrodes suspended in the liquid above the asbestos. A direct current at 110 v. was passed for a few minutes or several hours as required. The current strength varied from a small fraction of an ampere to two or three amperes. No attempt was made to study quantitatively the effect of variations in the current strength.

Objection may be raised that deposits near the electrodes could be accounted for by the droppings from these electrodes. This objection was met by using very compact powders and reporting only such deposits as appeared midway between the electrodes. Duplicates were also run with the U tubes inverted over beakers of the solution used. Deposits on the main electrodes could not possibly get into the membrane.

An important variation in the method of preparing the membranes consisted in packing the U tube with layers of different insoluble powders. A combination frequently used was asbestos plug, powdered glass, sulfur, silica and asbestos plug, in the order named. The yellow color of the sulfur aided the eye in marking boundaries. The deposit could generally be seen at the surface of the glass tube but in some cases the tube was broken at previously made file marks and the entire powder examined.

In addition to the results obtained by Braun, stenolytic deposits were secured with dilute water solutions of

Cu_2Br_2 in SiO_2 and glass powder
Cu_2I_2 in SiO_2 and glass powder
$CuSO_4$ in glass powder
Fehling's solution in glass powder
Na_2SnO_2 in glass powder
Na_2PbO_2 in glass powder
$(NH_4)_2MoO_4$ in S and SiO_2
$NiBr_2$ in glass powder
$MnCl_2$ in S

With a cracked glass tube prepared in the old way a distinct deposit of nickel peroxide was secured with a solution of nickel sulfate. Braun reports that he failed to obtain such a deposit. Another interesting result was the stenolytic discharge of bromide ion in glass powder and in sulfur. This was observed when electrolyzing cobaltous bromide solution several hours in sulfur and nickelous bromide in glass powder. In each case the bromine appeared around a small deposit of the metallic peroxide. The explanation is, of course, that the cobalt or nickel deposit became an intermediate electrode, with one end acting as cathode to the main anode and the other end as anode to the main cathode. The bromide ions were discharged at the anode end of the peroxide deposit. To test this explanation a short piece of platinum wire was imbedded in the sulfur membrane at some distance from the electrodes. Electrolysis of any bromide solution produced a quick appearance of bromine at the anode end of the platinum wire.

After a few hours, a distinct deposit of cobalt peroxide was secured with alternating current using cobaltous bromide in sulfur.

Coehn's theory of electrostenolysis leads one to expect that a compact membrane of any insoluble powder which is negative to water must be able to discharge positive ions during electrolysis. The list of observed deposits is short. A complicating feature is the property which some insoluble substances have of assuming a positive charge in some solutions and a negative in others. Sulfur, silica, glass, kaolin, most sulfides, and asbestos are negative to water; so the first deposit in such membranes must consist of metal or oxide. However, after such a deposit has begun it may cause the discharge of negative ions by its anode action. There are comparatively few insoluble substances positive to water. These include some metallic oxides and sulfides, lead sulfate, barium carbonate and chromium chloride (violet). Aluminium trioxide, lead sulfate and chromic chloride were tried without success. No negative metallic deposit was expected in them but it was thought possible that the bromide ion might be discharged and seen in such a white positive membrane as aluminium trioxide. None was obtained.

Summary.

The main purpose of this research was to develop a method for studying electrostenolysis on a larger scale than before. Some additional results of interest were obtained but no attempt was made to study variations in concentration, the solvent, voltage or current strength.

1. Deposits of metallic oxides and metals, due to electrostenolysis, were greatly increased by the use of capillary membranes in the form of glass tubes packed with such finely powdered substances as glass, sulfur and silica. The ease with which these tubes could be broken in sections

and the contents examined was a distinct advantage. By Braun's method, glass capillaries were the only ones possible but this improvement permits the use of any number of insoluble substances for a membrane.

2. In addition to the results obtained by Braun, electrostenolytic deposits were secured, by the new method, in water solutions of cuprous bromide, cuprous iodide, copper sulfate, Fehling's solution, sodium plumbite, sodium stannite, ammonium molybdate, manganese chloride and nickelous bromide. These results were secured with direct current at 110 v., but a deposit was also secured in a cobaltous bromide solution using alternating current.

A discharge of bromide ion was observed around an initial deposit of cobalt peroxide formed by electrostenolysis.

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THE ELECTRON CONCEPTION OF VALENCE.

BY STUART J. BATES.

Received February 27, 1914.

There is one point of considerable importance in connection with this theory to which it appears desirable to call attention in view of the recent discussions of this topic in THIS JOURNAL. Comparatively recent works in physics has caused physicists to reconsider the validity of the assumption that "every chemical bond formed between two atoms involves the transfer of a corpuscle from one atom to the other."[1] Thus Sir J. J. Thomson, who proposed and first developed the electron theory of valence, has, chiefly as a result of his investigation of positive rays, changed his opinion regarding the mechanism of the attraction between atoms. "We are led by these results to regard the electrical forces which keep the atoms in a molecule together as due not to one atom being charged positively and the other negatively, but to the displacement of the positive and negative electricity in each atom. Thus each atom acts like an electrical doublet, and attracts another atom in much the same way that two magnets attract each other."[2]

The objections which may be raised against the electron theory of valence are probably much less widely known among chemists than is the evidence in favor of it. It seems worth while to indicate the nature of a few of these objections without attempting to develop them here:

(1) It is difficult to conceive of the two atoms in the molecule of an elementary gas as hydrogen, or of the two methyl groups in ethane, as being so different from one another as would be the case if one half of the mole-

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[1] Nelson, Beans and Falk, THIS JOURNAL, **35**, 1810 (1913).

[2] J. J. Thomson, "Rays of Positive Electricity" p. 66, (1913), Longmans, Green & Co. See also *Phil. Mag.*, **24**, 249 (1912).