

in progress in the laboratory of the Chemical Institute of the University of Bonn, and we anticipate that the result will be the preparation of bodies having the general formula  $R'OPCl_4$ .

XII. "Note on the Electrodeposition of Alloys and on the Electromotive Forces of Metals in Cyanide Solutions." By SILVANUS P. THOMPSON, D.Sc., B.A. Communicated by Professor G. CAREY FOSTER, F.R.S. Received May 12, 1887.

It is known that the electrodeposition of such alloys as brass, bronze, and German silver is not practicable from mixed solutions of the sulphates or chlorides of the constituent metals, but can be accomplished by using cyanide solutions or neutral solutions containing cyanide of potassium in excess, thereby apparently departing from the law of Berzelius that out of a solution of mixed metals the least electropositive metal is deposited first.

To ascertain the cause of these facts the author has investigated—

(a.) The electromotive forces of a number of metals in aqueous solutions of cyanide of potassium.

(b.) The dependence of these electromotive forces, in particular those of copper and zinc, upon the degree of concentration of the solution.

(c.) The variation of the electromotive forces of copper and zinc in a standard solution of cyanide of potassium at varying temperatures.

(d.) The electromotive forces of zinc and copper in a "brassing" solution consisting of the mixed cyanides of zinc and copper, having excess of cyanide of potassium present, and their variation at different temperatures.

It is found that the effect of higher concentration of the cyanide solutions is invariably to increase the electromotive force of copper more than it increases that of zinc.

In a cold dilute solution of cyanide of potassium the electromotive force of zinc against carbon is 1.158 volt, while that of copper against carbon is 0.948 volt, or zinc is 0.210 volt higher than copper. In a boiling saturated solution of cyanide of potassium, the electromotive force of zinc against carbon is 0.768 volt, and that of copper against carbon is 1.300 volt; or copper is 0.532 volt higher than zinc.

It is therefore possible to construct a voltaic battery containing one metal only, namely copper, and one electrolyte only, namely an aqueous solution of cyanide of potassium, kept hot at the anode and cold at the cathode of the cell.

In cyanide solutions containing about the following number of

grams of cyanide to the litre, the following were the electromotive forces observed with a carbon cathode:—

Solution containing per litre					
99·4 grams.		191·4 grams.		1·18 grams.	
Metals at 18° C.					
Zinc .....	1·520	Copper .....	1·434	Zinc.....	1·13
Copper .....	1·425	Zinc.....	1·401	Brass .....	0·58
Brass .....	1·400	Brass.....	1·315	German silver ...	0·50
German silver ..	1·05	German silver ..	0·936	Lead .....	0·44
Gold .....	0·885	Gold .....	0·834	Copper.....	0·39
Silver .....	0·845	Silver .....	0·810	Silver .....	0·39
Lead .....	0·64	Lead .....	0·609	Gold .....	0·34
Iron .....	0·47	Iron .....	0·181	Steel .....	0·30
Steel .....	0·44	Steel .....	0·161	Iron.....	0·30
Platinum .....	0·27	Platinum .....	0·017	Platinum.....	0·14
Carbon .....	0	Carbon .....	0	Carbon .....	0

Several of the metals exhibit maximum electromotive force at an intermediate concentration.

The following figures were obtained for zinc and copper in solutions of cyanide of varying strengths at 17° C.:—

Grams per litre.	E.M.F. zinc.	E.M.F. copper.	Difference Z—C.
2·9.....	1·158	0·948	+0·210
5·9.....	1·167	0·967	+0·200
11·2.....	1·184	1·018	+0·166
23·8.....	1·221	1·058	+0·163
47·7.....	1·269	1·130	+0·139
95·5.....	1·303	1·220	+0·080
191·1.....	1·355	1·360	—0·005

In a mixed solution of cyanides of zinc and copper there is a neutral condition where the electromotive forces of zinc and copper are equal, and this neutral condition varies with the relative amounts of metal present, with the concentration of the solution, and with the temperature. The neutral temperature for a solution of given concentration is lowered by adding cyanide of potassium, and is raised by adding ammonia. The neutral point, however, is not well defined, the behaviour of copper being very uncertain; in general the electromotive force of clean copper in a cyanide solution rises, in some cases as much as 0·06 volt, in a few seconds after immersion, but is rapidly though temporarily lowered on agitation.

Since the degree of concentration of the solution greatly affects the electromotive force of the metal, and since in the act of deposition of a metal from its solution the concentration of the liquid around the cathode is reduced, owing to slowness of diffusion, it follows that in electrodeposition the counter electromotive force at the cathode will vary with the rate at which metal is being deposited, and will, therefore, vary with the current-density employed. And since, moreover, the variations in electromotive force due to differences of concentration are greater for copper than for zinc, it follows that in the deposition of brass from a mixed solution of cyanides of a medium concentration in which zinc is slightly more electropositive than copper, there will be a certain density of current with which the metals will be deposited in nearly equal quantities, whilst for weaker current-densities the less electropositive metal will be deposited in excess, and for stronger current-densities the more electropositive metal will be deposited in excess.

Hence to variations in the concentration of the electrolyte near the cathode are due the departures, observed with all currents except weak ones, from the law that out of a solution of mixed metals the least electropositive is deposited first.

XIII. "On the true Fructification of the Carboniferous Calamites." By WILLIAM CRAWFORD WILLIAMSON, LL.D., F.R.S., Professor of Botany in the Owens College and the Victoria University. Received May 17, 1887.

(Abstract.)

The true systematic position of the Carboniferous Calamites has long been a debateable subject, owing to the lack of satisfactory evidence respecting the character of their fructification. Some years ago, Mr. Carruthers and the late Mr. Binney expressed their conviction that *Calamostachys Binneyana* stood in that relationship to Calamites, a conclusion which the author was unable to accept; but in 1869 he obtained a fragment of a new Cryptogamic fruit, of which he published an account in the 'Memoirs of the Literary and Philosophical Society of Manchester.' The central axis of this Strobilus presented so many details of structure hitherto seen only in Calamites as convinced the author that it was the true fructification of these plants.

Many years elapsed before a second example of this interesting fruit was discovered, but seven or eight specimens of it recently found in a nodule from near Oldham, have come into the author's possession; these examples are in a sufficiently excellent state of