

unseparated matters. With aniline nitrate and cadmium below 10° C. aniline, benzene, and a little diazoaminobenzene.

It seemed probable from the foregoing that hydrazine nitrate might be more active than the ammonium salt and give some azides as by-products. In 1907 some hydrazine was made and absorbed in excess of nitric acid. Two salts were found to exist. The acid one was extremely deliquescent and decomposed slowly at ordinary temperatures in air, giving off nitric acid. The mono-nitrate resulting was found to crystallise well, although very soluble in water and deliquescent, but not so markedly so as the ammonium salt under similar conditions.

When Dr. Raschig visited this Society about two years ago I induced him to make for me some quantity of the mono-nitrate. This salt was purified by the addition of alcohol to a strong aqueous solution, the salt then crystallising out in an almost perfectly pure state.

Hydrazine nitrate melts without any decomposition at 70° C. and may be kept at 100° C. for a long time without change. When heated to about 200° C. in a vacuum tube the gases collected agreed almost exactly with the scheme, $4\text{NH}_2\text{NH}_2\text{HNO}_3 = 5\text{N}_2 + 2\text{NO} + 10\text{H}_2\text{O}$.

Heated in a closed vessel the nitrate explodes very violently, but under ordinary pressure merely burns rapidly. Contact with many kinds of oxidising agents, as permanganate, chromate, peroxide, causes inflammation.

A solution of this nitrate was found not to be active in contact with those metals which in the case of ammonium nitrate showed most marked activity. In fact, in most cases little or only very slight action has been observed. Possibly this slight action noticed in a few cases, as with zinc, may be due to the formation of a small quantity of ammonium nitrate.

The fused salt was found to be more active than ammonium nitrate but scarcely in the same manner. Zinc, copper, and most other metals causing a flaming decomposition at temperatures little above the melting-point of the salt—70° C.

Oxides, sulphides, nitrides, and carbides were found to behave in a similar manner, that is, simple inflammation with some oxidation of the substances in most cases. The two metals, cobalt and nickel, are to be obtained in two forms; one in which they have been completely melted and then worked in some manner, and in rough cubes or irregularly shaped pieces not completely fused through, just as they have been left by reduction from their oxides by some carbonaceous material.

Cobalt or nickel that had been thoroughly melted and worked into wire or plate behaved when added to melted hydrazine nitrate like all the other metals tried, viz., became a little oxidised and the hydrazine salt flared off.

On melting some of the nitrate and adding fragments of "commercial cube cobalt" a very violent action commenced, followed almost immediately by a severe explosion. This experiment has been repeated many times and it has been observed that not all the pieces or cubes in a 2 lb. lot of cobalt would explode, but a considerable percentage (about 40 per cent.). With similar nickel cubes the percentage showing this action was less—about 20 per cent. Lots obtained at different times showed like behaviour and variation. Pieces showing a light grey coloured fracture seemed as a rule the most active.

Nickel and cobalt reduced from the oxides by heating in hydrogen failed to produce any explosion.

One explanation of this action appears reasonable, that owing to some peculiar structure or state of division of the metal in the interior of these "cubes" some small amount of azide is formed, which on decomposing detonates some of the remaining hydrazine nitrate. Still this cannot be considered quite conclusive, for many times some unchanged nitrate was found spotted on the surrounding steel cylinder.

Also in many cases the effect was out of proportion to the quantity of nitrate employed and was, in fact, more violent when larger quantities of "active" metal was used.

I am much indebted to Lieut. Gibson, R.A., for many analyses and other help.

DISCUSSION.

Mr. W. F. REID said that the new reaction which had been shown to them was certainly one of a most mysterious nature and one that presented a great future. As one who had had a great deal to do with explosives, he would advise them not to try it in their laboratory until they had gained some experience in those matters. It was apparently very easy to make an experiment of that kind; but they wanted to know exactly the force of the material they were dealing with before they could safely carry out such an experiment.

Dr. E. FEILMANN said that there might be a possibility that the curious behaviour of the lump of nickel was due to occluded gas. He knew from experience how very common it was for such metals produced at high temperatures to contain a considerable amount of gas. It might be that acetylene or some other occluded gas would account to some extent for the mystery.

Mr. T. C. CLOUD said that nickel cubes consisted of a square shell of somewhat densely compact nickel enclosing a more or less spongy mass of the metal. It might be that the large amount of surface exposed in the interior brought about a very rapid decomposition with a large and sudden evolution of gas. That would not happen in the case of the rolled and dense form of the metal.

Mr. T. TYLER said he thought the observations of the previous speaker accounted very largely for some of the phenomena they had seen.

Professor HODGKINSON, in reply, said that, judging from his experiments, he did not think the cube form of nickel and cobalt contained any more gas than usual. It contained a little carbon in the form carbide, perhaps 1 per cent.; but he had tried carbide of nickel and it had no more action than the zinc. Nitrides of many metals could be made by heating them in ammonia. Nitrides when brought in contact with hydrazine nitrate, were merely converted into oxides. The metal was more porous than finely divided. At first he had seen it was porous, so he had reduced oxide of cobalt and oxide of nickel with hydrogen and cooled them carefully and they also had not exploded.

Manchester Section.

Joint Meeting with the Faraday Society held on Friday, April 4th, 1913.

ELECTROLYTIC METHODS FOR PREVENTING THE CORROSION OF METALS.

BY PROF. W. W. HALDANE GEE, M.Sc.TECH., B.Sc.

(Abstract.)

The corrosion of metals can be lessened or prevented in two ways: (1) By connecting the metal to be protected to a more electro-positive metal, so that a primary cell is produced; (2) by making the metal to be protected the cathode in an electrolytic cell supplied by an external electrical pressure. Various types of primary cell arrangements that could be employed in practice were classified. The efficiency of the cell for protection will depend on the current density at the cathode, and this will be controlled by the resistance of the cell and the effective voltage. The importance of overvoltage in determining the effective voltage was discussed. The history of Sir Humphry Davy's application of zinc and iron protection for the prevention of the corrosion of the copper sheathing of ships, and subsequent inventions for the protection of condensers and pipes were detailed. The patents of Harris and Anderson, in which aluminium alloys are used for the prevention of the corrosion of condenser tubes, were shown to be primary cell methods. The use of zinc in boilers involves a knowledge of the electrolytic resistance of the boiler waters and the effective voltage at temperatures from 150°—200° C., concerning

which there is great need of experimental data. The amount of zinc used in some marine boilers is as great as from 400—600 lb. of rolled zinc per annum. If the zinc is efficient in producing electrical currents then the average current may be from 17 to 25 amperes. It is obvious that such currents would be obtained much more economically by the use of a dynamo. The direct use of electrical currents has been the basis of a number of patents. Those of Mr. Elliott Cumberland were especially described. Iron anodes are placed in the water of the boiler, which latter is made the cathode. A low voltage of supply provided by a small motor-generator is used. The method has proved effective not only in preventing corrosion, but also in removing scale from the heating surface and preventing its formation. Experiments carried out at the Manchester School of Technology have shown that the current densities necessary to protect iron, copper, and other metals from the corrosion of fresh and salt water are of low value, and hence in the cases of boilers and condensers the annual cost of the electrical energy required is a small item. The chief cost will be in the renewal of anodes. Harris and Anderson have also applied electrical currents for the prevention of the corrosion of condensers. They find that a condenser with a cooling surface of 1025 sq. ft. requires only 2 volts and 2 amperes, and the special anodes used by them cost from £3 5s. per 1000 sq. ft. per annum. The use of electrical currents may also be applied in chemical works to prevent the corrosion of metallic screens and vessels from acid liquids.

THE NATURE OF OVERVOLTAGE.

BY J. I. CRABTREE, M.Sc., A.I.C.

(Abstract.)

It is well known that the voltage necessary to decompose a dilute acid electrolytically varies with the nature of the electrodes employed, that is, the metals involved possess different decomposition voltages for that acid, which are invariably in excess of that of platinised platinum. Let E_m and E_p be the decomposition voltages of a given acid with electrodes of a metal, m , and platinised platinum respectively. Then $E_m = E_p + \eta$. This excess value of the decomposition voltage η , over and above that observed with a platinised platinum electrode, is termed the "over-voltage" of that particular electrode. According as the gas separated occurs at the anode or cathode, we speak of the "anodic" or "cathodic" overvoltage. Le Blanc defines overvoltage as the excess of the back e.m.f. set up at the electrode over that given by a platinised platinum plate under identical conditions.

According to Tafel, the values for the cathodic over-voltage given by the different metals may be arranged in the following order of magnitude:—

Hg → Pb → Cd → Sn → Bi → Au → Ni → Pt. Cathodic overvoltage is influenced largely by the physical condition of the metal, the degree of hardness, and previous treatment, such as electro-deposition at different current densities.

The physical nature of the metal appears to affect other properties which appear to be allied to overvoltage. Thus Graham found that the amount of hydrogen occluded by platinum depends on the texture of the sample employed, and on its previous treatment. Platinum sponge adsorbs ten times the quantity of gas which an equal amount of massive platinum adsorbs.

The effect of thickness on overvoltage has been investigated by Pring by depositing films of metal of varying thicknesses on cathodes of different metals, and finding the overvoltage of the duplicate plate thus formed. Taking any one case, say lead deposited electrolytically on a nickel cathode, it was found that the overvoltage rose with increasing thickness of lead until a maximum was reached. This was assumed to be that thickness up to which the gas adsorbed by the electrode exerted an effect on the polarisation voltage. In the case of platinum this depth of metal appears to be approximately 4×10^{-6} mm.

In this connection the author made a series of experiments by "sputtering" a metal on to a glass electrode, by

placing the same near the anode (of the same metal as was required on the glass) in an exhausted cathode ray tube and passing a strong discharge.

Excellent deposits of microscopic thickness were obtained, but these invariably peeled off the glass when employed in the electrolytic vessel.

Application of overvoltage.—Of the numerous instances where a particular property of a metal may be attributed to its overvoltage may be mentioned the effect of the nature of the electrode employed on the efficiency of an electrolytic oxidation or reduction process; and the possibility of separating two metals in solutions, whose decomposition voltages are almost equal, by choosing as cathode a metal which gives to hydrogen a decomposition voltage intermediate between that of the two metals to be separated.

In the case of the corrosion of a metal its overvoltage may be of importance as either: (a) Having a tendency to retard the deposition of hydrogen or oxygen on its surface, which might either assist or prevent corrosion; (b) By setting up a high back e.m.f., which would diminish the effect of a decomposing current in cases of corrosion due to electrolysis; (c) by assisting or preventing the solution of a metal. The part played by overvoltage in this case is made clear by considering the condition which must hold in order that a metal may dissolve in an acid and evolve hydrogen. If the overvoltage is large, no solution of the metal can occur. This is apparent with amalgamated zinc, where, owing to the high overvoltage of the mercury, no solution of the zinc takes place, the alloy assuming the overvoltage of the external metal. Similarly iron covered with zinc or tin does not rust, since the overvoltage is raised.

Zinc covered with platinum dissolves readily, since the overvoltage is lowered. As a means of preventing corrosion, and therefore of raising the overvoltage of the metal in question, it is necessary to coat this with either lead, tin, cadmium, or zinc, which metals have high overvoltages. The reason for the extensive employment of zinc and tin for this purpose is therefore apparent.

AN ELECTROLYTIC THEORY OF THE CORROSION OF IRON.

BY B. LAMBERT.

(See this Journal, April 30th, 1912, page 428.)

DISCUSSION.

Mr. J. H. SILVERWOOD explained, by means of lantern slides, the advantage of protector blocks in water tube ends of condensers, every tube being in electric contact with the tube plates. By this means corrosive action, instead of attacking the tubes, travelled to the tube plate, and so on to the protector block which, being an alloy electropositive to the material of which the tubes were made, took the corrosion instead of the tubes. The cost of upkeep of the tube protector was about 2d. per indicated horse power per annum. In the case of a steamer plying between St. John's, Halifax, and Manchester, the owners were re-tubing the condenser, top half one year, and the bottom half the following year, there being some 800 tubes in each half, and five to six tubes corroding each journey. A protective system had been installed for about two years, and so far he had not heard that a single tube had failed. Another protective system, working on the River Mersey, gave a saving of about 93 per cent. of the tubes. Corrosion took place chiefly on steamers plying on estuary water, or in the case of surface condensers in electricity works or others which were using estuary water, but some cases were difficult to explain. The steamers "Strathmore" and "Minerva," plying on the Clyde, practically performed the same duties, so that apparently the conditions were similar. In the case of the "Strathmore," after she had been in service for six months, half a dozen tubes failed, and then the rest followed very quickly, so a protective system was applied, and a certain amount of corrosion was arrested. None of the "Minerva's" tubes failed, and in order to ascertain the reason about 40 tubes were borrowed from the "Minerva" and placed in the