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PART 2.

MASS ANALYSES OF MUNTZ'S METAL BY ELECTROLYSIS, AND SOME NOTES ON THE ELECTROLYTIC PROPERTIES OF THIS ALLOY.

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(*A Paper read before the Faraday Society on Monday, January 30, 1905,
PROFESSOR A. K. HUNTINGTON in the Chair.*)

Towards the end of 1903 the author was asked by the Muntz's Metal Company, Ltd., to devise a method of accurately determining the copper contents of Muntz's metal at such a speed as to enable the management to utilise the results in the ordinary course of manufacture. The difficulties were many, viz., the large number of analyses required, the extreme accuracy necessary, the necessity of working during the night as well as during the day, and finally the *conditio sine qua non* that the results must be obtained within twelve hours of the time of casting. A careful examination shows that these difficulties are fairly great. In the ordinary course of events 40 to 60 "heats" of metal are cast every twenty-four hours at the Company's works. The same number of analyses have to be made, without interfering with the capacity of the laboratory to cope with the numerous analyses of other mixtures produced in the factory. Hence the scheme must be such as to enable us to make at least 100 copper determinations in the twenty-four hours. With regard to the accuracy, the limits of useful copper contents are from 60.0 per cent. copper to 62 per cent., and within these limits there are four classes of metal behaving differently as to rolling temperature. Towards these limits the metal is extremely sensitive to over-heating in the one case, and to under-heating in the other. A metal containing 62.0 per cent. of copper can be rolled at an elevated temperature; one containing 62.25 per cent. would not stand the ordinary treatment at all. Hence we must have a mean probable error of not more than ± 0.1 per cent. On the other hand, metal with less than 60 per cent. of copper behaves towards sea water in a way which is highly undesirable. It is characterised by

preferential dissolution of zinc, which occurs very rapidly. The difficulties, so far, might be met by the odometric method suitably modified, but when it comes to night work and work in bad light, this method fails entirely. Even very good, and consequently well-paid operators cannot use it unless the conditions of light are very favourable, and one is in every case dependent upon the operator's more or less delicate sense of colour. I tried it, as a matter of fact, but with very unsatisfactory results. To obtain speed in this case would mean the employment of a considerable number of operators who have had a fair experience. These and other considerations made me decide to adopt the electrolytic method. In carrying out my design, I had an absolutely free hand, and I am greatly obliged to the directors of Muntz's Metal Company, Ltd., for putting no restriction in my way as to cost of plant, etc., which, as will be seen later on, was fairly considerable. I shall now proceed to describe the electrolytic plant in detail, and afterwards its mode of working.

I. THE ELECTRODES.

As I had to deal with unusual current densities, I decided to increase both the anode and cathode surfaces to the utmost limit compatible with moderate weight. From this reason I chose a very fine platinum wire gauze as the material. The gauze was made from No. 36 B.W.G. hard platinum wire, ninety meshes to the inch. To support this delicate fabric, a framework of stout platinum wire was designed in the case of

FIG. 1.

the cathode. This framework serves another purpose as well, viz., it makes the current distribution even. Fig. 1 represents a pair of electrodes, *a* is a cathode and *b* an anode. The cathode is very much the same as an ordinary gauze cathode with the exception of the above-mentioned framework. The anode, however, differs from most constructions by having a cylindrical part of extensive surface which, when in use, is concentric with the cathode. The pole wire of the anode is fastened to the bottom ring at *c*. This way of connecting electrolytic combinations serves two purposes. By having the two

points of maximum P.D. at the upper and at the lower end of each of two concentric electrodes, it may be assumed that the current distribution will be very even, as when such an arrangement is used, the P.D. between any two radically opposed points in any horizontal section is, theoretically and practically, everywhere the same. Secondly, the arrangement offers no obstacle to the rapid removal of the cathode. I have in fact resorted to the plan employed for many years by the E.P.S. Company in coupling accumulator plates. Thirty pairs of electrodes are at present in use in our laboratory,

FIG. 2.

all being of this type. They were made by Messrs. Johnson and Matthey. Fig. 2 shows a couple of these electrodes in use. I always utilise as a containing vessel the same kind of beaker, viz., 500 c.c. Jena beakers. They are stouter and stronger than ordinary Bohemian glass beakers, besides being less affected by changes of temperature. The electrode holders are ordinary Classen stands, but modified. To force the operators to place the beakers neatly, and to avoid accidental short circuits, the table is provided with turned wooden cups (*a*), which are firmly screwed down. The stands are also screwed

FIG. 3.

down to avoid accidents, which might occur from the simple reason that no less than twenty-five pairs of electrodes are worked on a table 15 feet 6 inches long. To cover the beakers, I use stout watch-glasses, provided with a slot (Fig. 3). Ordinary watch-glasses treated in this way are too delicate and

fragile, hence I have lately resorted to watch-glasses 4 mm. thick. There is no disadvantage connected with this plan, as heating of the electrolyte is unnecessary.

2. THE ELECTRICAL ARRANGEMENTS.

I have tried to arrange matters in conformity with the best accumulator practice. To accomplish this, use has been made of a fair number of cells, which are always charged in series and discharged in independent couples of two cells in series. The plant consists of six pairs of the Chloride Company's RP₉ cells in lead-lined wood boxes, each pair supplying current to five pairs of electrodes. Fig. 4 is a diagram of the connections of two sets of five pairs of electrodes. The batteries B₁ and B₂ are connected to the conductors L₁ and L₂, and L₃ and L₄ respectively.

FIG. 4.

The conductors are enclosed in wood casing, screwed down to the table. Parallel branches run to the different electrodes, a₁ and c₁, a₂ and c₂, etc.; but it should be pointed out that the main conductors, L₁ and L₂, and L₃ and L₄, are insulated from each other between the sets, so as to prevent the batteries from discharging into each other. In each one of the secondary branches there is a resistance, R₁ or R₂, etc. These resistances can be shunted at S₁, S₂, S₃, etc. All the resistances are made from No. 20 nickelin wire, stretched on porcelain bobbins in front of the table. Hence they can easily be got at, and this is convenient for repairs, which have frequently to be made when electrolytic work is carried on continuously.

Fig. 5, which is a photograph of the main installation of twenty-five pairs, gives a good idea of the exterior of the plant. Besides the above, I might mention that the accumulators are charged from the light mains, and independently of the discharge, as may be seen from the scheme of connections.

Fig. 5.

3. ANALYSIS OF MUNTZ'S METAL.

The process is the simplest one possible. One gramme of the alloy is dissolved in 20 c.c. nitric acid, 1·2 sp.g., and the solution is heated on a sand bath till the red fumes disappear; 300 c.c. of distilled water are afterwards added, and the beaker is put in its place on the electrolytic table. The electrodes are put in, and electrolysis is proceeded with. Two current densities are employed, viz., 0·5 amperes or 2·0 amperes, for the electrodes as described. With the low current-density all the copper is deposited after twelve to fifteen hours; this is confirmed by taking out a sample and testing it with H_2S water. The cathode is then taken off very swiftly and it is immediately plunged into a large beaker containing distilled water. After washing it carefully, it is dipped into absolute alcohol and dried in a steam oven, and eventually it is cooled in the open air and weighed. The high current-density is obtained by shunting the resistances at S, etc. (Fig. 4). The time necessary for complete deposition of the copper in this case *is only three hours, and the deposit obtained is perfectly adherent to the cathode.* In other respects the operations are similar. The theoretical loss, which must occur when the cathode is taken out in the manner described, was carefully investigated, and found to be of so small a magnitude as to be negligible. That the copper is fully deposited is patent from the fact that the remaining solution gives no reaction for copper with any known reagent. As a matter of fact we may distinguish between three distinct phases of the reaction: (1) Copper deposition and ammoniacal reduction of nitric acid; (2) ammoniacal reduction *per se*; (3) deposition of zinc in some form or another. Phase 2 occupies a considerable time, and during that time the removal of the cathode takes place. It has very often been stated that the deposition of copper in the presence of zinc is incomplete, and many theoretical considerations would lend support to this statement. I think, however, that in the case under consideration, where the overlapping phase 2 occupies a long time, and is unaccompanied by *metal deposition*, a perfect separation is theoretically possible. That it is so practically is demonstrated by our daily work. Some metals do interfere with the accuracy of electrolytic copper determinations in nitric acid solutions, amongst others arsenic and nickel. When analysing arsenical copper I find that perfectly accurate results are obtained, if the arsenic be removed by means of metallic zinc in dilute nitric acid solutions before the electrolysis takes place. If this be omitted, the results are invariably high. Nickel will deposit with copper to some extent, especially if the alloy contains phosphorus, and in that case chemical separations must be resorted to as an initial step; but even then I prefer to weigh both copper and nickel as metallic deposits for the sake of accuracy.

The usual run of work during twenty-four hours may be said to be as follows: At 8.30 a.m. the two men, who do day work with twenty-five pairs of electrodes, find twenty-five analyses going. They test them, wash down the cover glasses, etc. At 9 a.m. one man takes out the cathodes, and the other one drills the morning's samples by means of a self-feeding American hand-drilling machine. He afterwards assists in taking in cathodes to be weighed by the first man. The weighing operations are finished by 10 a.m., and the results are immediately calculated on a Fuller's slide rule and entered in the firm's books. At 10.30 a.m. the analysis results are compared with the results of the rolling tests in the mill. Whenever there is a discrepancy orders are issued to hold the heat of metal back for analysis. In the meantime the cathodes are stripped by putting them all together in a large accumulator box full of nitric acid. They are afterwards washed, ignited,

TABLE I.

Original Analysis.	Re-Analysis.	Δ Cu.	Original Analysis.	Re-Analysis.	Δ Cu.	Original Analysis.	Re-Analysis.	Δ Cu.
Per Cent. Cu. 60'60 60'26 60'32 60'48 62'13 62'04 62'32 60'61 60'83 60'32 60'36 60'60 60'19 62'06 62'03 60'80 60'42 62'25 61'46 61'57 61'81 60'89 61'15 61'65 62'02 61'12 60'62 60'41 60'52 61'16 60'59 60'63 60'30 61'31	Per Cent. Cu. 60'67 60'16 60'32 60'46 62'15 61' 6 62'10 60'63 60'98 60'45 60'39 60'49 60'27 62'14 62'06 60'91 60'66 62'47 61'48 61'51 61'60 60'93 61'15 61'76 61'94 61'13 60'67 60'22 60'51 60'95 60'67 60'39 60'47 61'40	Per Cent. Cu. + 0'07 - 0'10 Nil. - 0'02 + 0'02 - 0'08 - 0'22 + 0'02 + 0'15 + 0'13 + 0'03 - 0'11 + 0'08 + 0'08 + 0'03 + 0'11 + 0'24 + 0'22 + 0'02 - 0'06 - 0'21 Nil. + 0'11 - 0'08 + 0'01 + 0'05 - 0'19 - 0'01 + 0'05 - 0'21 + 0'08 - 0'24 + 0'17 + 0'09	Per Cent. Cu. 61'00 61'35 60'29 60'37 60'60 62'13 62'11 61'96 61'91 61'37 61'57 61'78 61'88 60'47 60'42 60'47 60'30 60'71 60'89 60'21 60'50 60'39 60'70 60'08 60'16 60'02 59'75 60'36 60'46 60'51 60'41 60'25 60'11 61'86	Per Cent. Cu. 61'21 61'27 60'52 60'40 60'61 62'02 61'90 61'94 61'95 61'53 61'66 61'78 61'92 60'55 60'52 60'58 60'38 60'77 60'66 60'41 60'58 60'39 60'51 60'20 60'24 60'02 59'71 60'62 60'46 60'37 60'32 60'07 60'06 61'61	Per Cent. Cu. + 0'21 - 0'08 + 0'23 + 0'03 + 0'01 - 0'11 - 0'21 - 0'02 + 0'04 + 0'16 + 0'09 Nil. + 0'04 + 0'08 + 0'10 + 0'11 + 0'12 + 0'06 - 0'23 + 0'20 + 0'08 Nil. - 0'28 + 0'12 + 0'08 Nil. - 0'04 + 0'26 Nil. - 0'14 - 0'09 - 0'18 - 0'05 - 0'25	Per Cent. Cu. 61'32 60'29 60'02 61'32 60'29 61'36 60'61 60'74 60'30 60'80 60'74 60'86 61'77 62'09 60'48 60'56 60'02 60'25 61'98 61'35 61'90 60'84 60'83 60'68 61'50 61'61 60'08 60'50 60'35 60'53 60'15 60'07 60'52	Per Cent. Cu. + 0'05 - 0'05 + 0'22 + 0'05 - 0'05 - 0'01 - 0'19 - 0'18 + 0'29 - 0'06 + 0'07 - 0'11 + 0'06 - 0'26 - 0'03 + 0'23 + 0'15 Nil. - 0'08 - 0'01 - 0'16 - 0'09 + 0'15 - 0'26 + 0'06 - 0'02 - 0'15 + 0'06 - 0'01 - 0'01 + 0'13	

and weighed ready for the next samples. By proper scheming the fresh lot of samples is ready for electrolysis at noon, when another lot of samples arrives. These are drilled, weighed in, and dissolved before the electrolysis of the morning's samples is at an end, viz., at 3.30 p.m. The cathodes are again washed, dried, and weighed, and the results are again compared with the mill tests at 5 p.m., and orders issued for eventual re-sampling, etc. The noon samples have in the meantime been put *in situ*, the cathodes stripped and weighed, and the electrolysis can be started at 5.30 p.m., when the day men leave. As a general rule only one man works during the night, taking off the noon samples and putting on those which arrive at 5.30, which he leaves with the low current to be taken off next morning at 8.30. The 5.30 samples and the noon samples are reported upon together in the morning. In this way seventy-five samples are handled in twenty-four hours, and the results are, on the average, only twelve hours behind the casters. Should an unusual pressure of work come on, we can manage one hundred by putting one of the senior assistants to help the night man. Five more pairs of electrodes are worked on another table in connection with the more exhaustive metal analyses, which frequently occur.

4. THE PROBABLE ACCURACY OBTAINED.

As mentioned above, a number of re-analyses occur in our work. They are never done by analysing part of the original test-piece, but by drilling one of the "strips" represented by this test-piece and analysing the drillings. In this way the differences include, besides the inherent analysis errors, the error due to possible lack of uniformity of the metal. In the table on page 124 I give the results of one hundred repetitions taken from the analysis book in sequence. It will be seen at once that the differences are extremely small.

The maximum difference was 0.29 per cent.

„ minimum	„	„	± 0
„ average	„	„	0.1048 per cent.

Hence the probable difference or error—

$$\pm 0.0706 \text{ per cent.}$$

From this we may conclude that the mixing of the separate heats of brass is incredibly uniform, and that the electrolytic method yields most reliable results. There is, of course, a permanent error, viz., the results obtained are always too low to a very slight extent, probably < 0.05 per cent. This is in our case an advantage, as no mistake is likely to occur in the rolling test when the copper percentages are too high, whereas mistakes are very common at the lower limit. I have known cases where a whole series of rolling tests passed low percentage metal into the mill, and *vice versa*, it frequently happens that perfectly good metal does not pass the rolling test. As this deceives the casters, there is every likelihood that one or two accidental mistakes in judging the metal by the rolling test will be followed by unintentional production of bad metal. Hence the justification of analyses on a large scale.

5. THE UTILITY OF MASS ANALYSES.

Since the 1st of January, 1904, over 11,000 copper determinations have been made by us in this way, and this naturally raises the question as to the object achieved by such an undertaking. To illustrate this I shall shortly give some statistical figures relating to the average composition of Muntz's

metal during June and July, 1904, when the effect of the work's control could be seen, after six months' working. To begin with, it must be remembered that Muntz's metal is produced by melting copper in reverberatory furnaces, afterwards adding zinc slightly in excess of the desired quantity, or, to use the trade term, "speltering." After "speltering" the "heat" is agitated, and finally tapped in a mixing vessel, from which it is ladled into pouring vessels, and subsequently cast into "strips." You could naturally expect no reliable results from such a process, where the zinc is burning away continuously, and where everything depends upon the judgment of the casters, in as far as tapping at the right moment is concerned. When the more or less unreliable "rolling test," which depends upon the appearance of hot rolled strips, was used exclusively, re-melting had to be resorted to very frequently. After six months of analytical control, matters altered very considerably. Re-melting became very rare indeed, and the casters' judgment became very much improved, after they had realised that the analytical control gave them an infallible guidance. Hence the principal achievement was a moral effect upon the casters, who could always see which way things turned. The double control by the rolling test, in combination with analysis, serves the purpose of indicating cases of actual mistakes, which have been very few indeed, viz., less than one dozen in over 11,000 cases. We aim at producing metal containing from 60.50 per cent. to 61.50 per cent. of copper—the outside limits being respectively 60 per cent. and 62 per cent. The following are the figures for June and July :—

June, 1904.

		Number of Heats.	Percentage of the Whole.
Below 60 per cent. of copper ...	...	None	or 0.00 per cent.
From 60.00 to 60.50 per cent. of copper ...	...	103	„ 13.34 „
„ 60.50 „ 61.50 „ „ „	...	643	„ 83.28 „
„ 61.50 „ 62.00 „ „ „	...	25	„ 3.24 „
Above 62 per cent. of copper ...	...	1	„ 0.14 „
Total	...	772	heats 100.00 per cent.

July, 1904.

Below 60 per cent. of copper ...	...	3	or 0.27 per cent.
From 60.00 to 60.50 per cent. of copper ...	...	114	„ 10.30 „
„ 60.50 „ 61.50 „ „ „	...	876	„ 79.13 „
„ 61.50 „ 62.00 „ „ „	...	98	„ 8.85 „
Above 62 per cent. of copper ...	...	16	„ 1.45 „
Total	...	1,107	heats 100.00 per cent.

It will thus be seen that the most desirable composition is obtained in over 80 per cent. of the cases, whereas the metal which has to be remelted is less than 2 per cent. of the whole. To anybody accustomed to manufacturing losses this result is eminently satisfactory. As I can state that the averages continue to be as good, there is no doubt that something is achieved, especially as each heat represents half a ton of metal. The commercial aspects of the case have, however, very little to do with the object of this paper; but as the whole question leading to the work was one of manufacturing economy, I may be forgiven for having made this departure in demonstrating the practical utility of a scheme like the one under treatment.

6. THE ELECTROCHEMICAL PROPERTIES OF MUNTZ'S METAL.

In this section I shall only foreshadow the probable issue of an extensive research, which is at present carried on by me. Muntz's metal was originally, and is now to a great extent, employed as sheathing for the protection of woodwork against the action of certain mollusca and algæ which breed in the sea. To be successful it must dissolve in sea water by electrolytic action to a sufficient extent to render the surface poisonous, but sufficiently slowly to make its use economical. The optimum must occur when the two constituents, copper and zinc, dissolve at exactly the same rates in which they occur in the alloy, during as great a part of the life of the plate as possible. By this means only the metal will remain of similar composition throughout its life, or the greater part thereof. To treat this problem mathematically is not difficult, but unfortunately the electric constants for most metals are only known approximately. I shall, however, show that a very good approximation of the truth can be arrived at with figures at our disposal. We can suppose that the electrolytic dissolution rate is directly proportional to the heat of formation of the ultimate compounds, and to the electrical conductivities of the metals which dissolve. As the specific conductivities are given per volume, these factors have to be divided by the densities of the metals in question. In the case of copper and zinc in sea water, we may take the ultimate products as zinc chloride and cuprous chloride. The electrolyte, principally sodium chloride, being highly dissociated, there is no vital objection to employing the thermochemical reasoning on total work, without introducing Nernst's theory of partial dissolution pressures. We may proceed to calculate as follows :—

Copper. Specific gravity $\delta_{\text{Cu}} = 8.9511$. Swan & Rhodin, *Proc. Royal Soc.*, lvi., pp. 70 and 71.

Specific conductivity $k_{\text{Cu}} = 55.86$. Roberts Austen, *Introduction to Metallurgy*.

{ Molecular $w_{\text{Cu} \rightleftharpoons \text{Cl}} = + 35.4$ Cal. Biedermann, *Chemiker Kalender*,
 { Formation heat 1904.

Zinc. Specific gravity $\delta_{\text{Zn}} = 7.15$. Roberts Austen, *ibid.*

Specific conductivity $k_{\text{Zn}} = 16.92$. Roberts Austen, *ibid.*

{ Molecular $w_{\text{Zn} \rightleftharpoons \text{Cl}_2} = + 113.0$ Cal. Biedermann, *ibid.*
 { Formation heat

Optimum percentage of copper : x ;

„ „ zinc : $100 - x$.

From the above reasoning the optimum occurs when—

$$\frac{x}{100 - x} = \frac{2(w_{\text{Cu} \rightleftharpoons \text{Cl}}) \cdot k_{\text{Cu}}}{\delta_{\text{Cu}}} : \frac{w_{\text{Zn} \rightleftharpoons \text{Cl}_2} \cdot k_{\text{Zn}}}{\delta_{\text{Zn}}} \quad (1)$$

Inserting the above values, we get—

$$\frac{x}{100 - x} = \frac{2 \cdot 35.4 \cdot 55.86 \cdot 7.15}{8.9511 \cdot 16.92 \cdot 113} ;$$

$$\begin{array}{l} x = 62.296 \text{ per cent. copper} \\ y = 37.704 \text{ „ zinc} \end{array} \quad \} \quad \cdot \cdot \cdot \cdot \cdot \quad (2)$$

In the above we have supposed the copper to dissolve as—

If we now suppose the reaction—

to take place, we have only to substitute the formation heat—

for $2(w_{\text{Cu}} \rightleftharpoons \text{Cl})$ in formula (1). The numerical results then become—

$$\left. \begin{array}{l} x = 59.326 \text{ per cent. of copper} \\ y = 40.674 \text{ „ „ zinc} \end{array} \right\} \dots \dots (3)$$

As the oxygen quantities in the sea water vary considerably, it may be assumed that sometimes the cupric and sometimes the cuprous reaction takes place. The mean between (2) and (3) ought to represent the best all-round composition of Muntz's metal. The mean values are :—

$$\left. \begin{array}{l} 60.811 \text{ per cent. of copper} \\ 39.189 \text{ „ „ zinc} \end{array} \right\} \dots \dots (4)$$

This agrees fully with practical experience, which can be seen from the above results of mass analyses—we call metal containing from 60.80 to 61.25 per cent. “good,” and we strive to produce metal of such a quality. It has also been observed that for tropical waters, which contain less oxygen and more reducing organic matter, thus favouring the cuprous reaction, a higher percentage of copper is necessary, whereas for temperate and arctic waters a less rich alloy stands very well. The old theory of structural peculiarities as the cause of the peculiar properties of Muntz's metal falls to the ground from the reason that the dissolution is truly electrolytic, thus depending upon impacts of ions or magnitudes infinitely smaller than the component parts of the structure of the alloy. That the structure favours even exfoliation is a contributory factor of favourable nature, but it does not explain the behaviour of the metal in sea water. The above reasoning gained its simplicity from the fact that we had only to find a ratio, and not the actual magnitudes in absolute measure. I am, however, making investigations with a view towards this object. The dissolution velocities of zinc have been studied, and subjected to mathematical analysis most successfully by my friend Dr. Wilhelm Palmær, of Stockholm (vide *Zeitschrift für Physikalische Chemie*, vol. 39, pp. 1, etc., and vol. 45, pp. 182, etc.). As a measure of the dissolution velocity he employed the mensuration of hydrogen, evolved per unit of time, when zinc dissolves in dilute acids. In our case dilute acids and low temperatures would yield too small velocities for convenient mensuration, hence I determined in the first instance to employ fairly concentrated hydrochloric acid (10.037 N). I prepared some wire from Muntz's metal, containing 60.50 per cent. of copper, approx. 0.25 mm. diameter. Pieces of this wire were introduced into an apparatus fitted with 10.037 HCl. The lower part of the apparatus was of test-tube shape, with a side tube for introducing the wires and to receive the stopper belonging to a levelling vessel. This part of the tube was immersed in a boiling water bath. An eudiometer tube was fused to this test tube, and surrounded with a water jacket to allow the gas to be measured at a fairly low temperature, varied as little as possible. Fig. 6 is a graphical representation of the results of two pairs of experiments, and they puzzled me for a long time.

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Experiment I.—Surface of wire	: 1 cm. ²
Weight „	: 0.0562 grammes
Mean temperature of H ₂	: 19.74° C.
Experiment II.—Surface of wire	: 1 cm. ²
Weight „	: 0.0562 grammes.
Mean temperature of H ₂	: 23.15° C.
Experiment III.—Surface of wire	: 4 cm. ²
Weight „	: 0.2226 grammes.
Mean temperature of H ₂	: 19.15° C.
Experiment IV.—Surface of wire	: 4 cm. ²
Weight „	: 0.2214 grammes.
Mean temperature of H ₂	: 21.04° C.

We see that the difference between Experiments I. and II. is confined to a difference between the temperature of the top part of the apparatus, where the hydrogen was measured, and that of the water bath surrounding the

FIG. 6.

bottom part. Evidently case II. favoured more rapid convection of heat, thus making the average temperature such as to favour a slower dissolution velocity. In cases III. and IV. this difference is less marked, as is also the difference between the results. But why should there be such a difference between the two *sets* of experiments? From the simple reason that in Experiments III. and IV., with wires of four times the surface of those in Experiments I. and II., the total bulk of hydrogen evolved per unit of time is greater, thus favouring a more rapid mechanical convection of heat through the stirring effect of the gas bubbles. Hence the mean temperature surrounding the wires in Experiments III. and IV. must have been considerably lower than in Experiments I. and II. As a consequence of these defects in my experimental arrangements, I arrived at four different *sets* of dissolution velocities at four different temperatures in the neighbourhood of $100^{\circ}\text{C}.$, instead of only one set. Although these measurements, from the above and other reasons, are far from critical, we may draw several interesting conclusions from the curves. Curves I. and II., which represent nearly complete dissolution of the wires, show that the velocity is remarkably constant after once having arrived at a maximum. The very gradual decrease of speed is accountable for in this way. We know that the copper and zinc of Muntz's metal dissolve at such a rate as to keep the composition fairly constant, and hence the specific conductivity the same. From this we must conclude that the surface must remain fairly constant, viz., as the total dimensions of the wire decrease structural development of the surface must take place at approximately the same rate. There is, however, a very gradual preferential dissolution of zinc, which makes the specific conductivity gradually decrease at a somewhat more rapid rate than the extra increase of surface gained by increased porosity. Hence a decrease of dissolution velocity, which, of course, finally gets influenced by the decrease of all the magnitudes involved. Curves III. and IV. show, however, that there is a temperature in the neighbourhood of $100^{\circ}\text{C}.$, where an astounding constancy of dissolution speed obtains, and where thus a state of dynamical equilibrium prevails. That such a state of equilibrium is possible in the case of an alloy is in itself very interesting, and promises a future development of a very important nature, viz., an elucidation of the molecular work in alloys, and its subdivision in component parts. I have prepared material and constructed apparatus for an exhaustive research on the subject, but the progress is naturally slow. The mere preparation of pure alloys is exceedingly difficult, but as impurities greatly influence the phenomena in question (*vide* Palmær, *loc. cit.*), it is desirable to investigate truly binary alloys in the first instance. There are, furthermore, the difficulties of constructing the apparatus in such a manner as to obtain a correct knowledge of the temperature which prevails when the dissolution actually takes place. We shall also re-determine all the necessary physical constants of the alloys. All this takes time, but I hope shortly to be able to make further communications on the subject.

December 1, 1904.

APPENDIX (*Added January 27, 1905.*)

Since writing the above I have continued the experimental research on the subject with very interesting results. The apparatus is rather too complicated to be described in this Paper, but the following details might be mentioned. Considering the importance of keeping the temperature constant the dissolving vessel was surrounded by a large quantity of water,

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heated by gas, regulated by a thermo-regulator. The water was agitated by means of a stirrer, worked by an electromotor. The thermo-regulator was actuated according to Professor Ostwald's suggestion by means of a saturated solution of calcium chloride, and it was found by experiment to keep the temperature constant within 0.1° C. The working temperature chosen was 80° C., and the concentration of the acid the same as before, viz. 10.037 N. The hydrogen was collected over 10 per cent. KOH solution to eliminate the partial pressure of HCl gas passing through the capillary connections. The wire used analysed as follows :—

Copper	...	...	62.000 per cent.
Iron	...	...	0.131 " "
Zinc	...	...	37.860 " "
			<hr/>
			100.000 per cent.

No lead or any other metal was present. The alloy was made by myself from pure copper and electrolytic zinc. It was drawn into wire in the laboratory. To begin with two parallel experiments were made, exposing in one instance 4 sq. cms. of wire, and in the other 2 sq. cms. The results were as follows :—

ACTING TEMPERATURE 80.0° C.

	Experiment 5.		Experiment 6.	
Weight of wire	...	0.4397 grammes	...	0.2103 grammes.
Surface	...	4 sq. cms.	...	$4 \times \frac{0.2103}{0.4397}$ sq. cms.
Barometric pressure	744.10	mm.	...	758.4 mm.

VOLUME OF HYDROGEN OF 760 MM. AND 0° C. EVOLVED PER 10 MINUTES PER SQ. CM. AREA.

	Experiment 5.		Experiment 6.	
After 20 minutes	1.00	cc. ...	1.15	cc.
" 30 "	1.02	" ...	1.20	"
" 40 "	1.05	" ...	1.24	"
" 50 "	1.01	" ...	1.13	"
" 60 "	1.03	" ...	1.03	"
" 70 "	1.05	" ...	1.05	"
" 80 "	1.04	" ...	1.05	"
" 90 "	0.98	" ..	1.00	"
" 100 "	1.02	" ...	0.95	"
" 110 "	—	...	0.90	"
" 120 "	—	...	0.92	"
Mean velocity	...	1.022 cc.	...	1.056 cc.

It will thus be seen that the mean velocities for the smaller wire are considerably higher than those for the larger one, and this in spite of the fact that the barometric pressure during Experiment 6 was higher than during Experiment 5. The way in which diminished pressure influences the results will be elucidated later on. At the end of Experiment 6 only 0.0964 grammes of the wire remained undissolved. This was analysed and found to contain 59.96 per cent. of copper, thus proving that copper dissolves by preference under these peculiar circumstances, a thing which I concluded from theoretical reasons before these more critical measurements were made. Shortly after these experiments were concluded, I repeated Experiment 5, when the

barometric pressure was unusually low, 731.6 mm. at 14.5° C. The results were considerable higher, as can be seen from the following table. That this should be so is fairly self-evident, as the hydrogen will disengage itself more easily from the surface of metal when the pressure is low. The magnitude of this influence is, however, surprising.

EXPERIMENT 7.

Weight of wire	...	...	0.4365 grammes.
Surface „	...	...	3.97 sq. cms.
Barometric pressure (corr.)	...	...	729.77 mm.

Volume of hydrogen evolved per sq. cm. area calculated at 760 mm., and 0° C., per 10 minutes :—

After 20 minutes	...	1.11 cc.	
„ 30 „	...	1.17 ₅ „	
„ 40 „	...	1.23 „	
„ 50 „	...	1.14 ₅ „	
„ 60 „	...	1.09 „	Acting temperature 80° C.
„ 70 „	...	1.10 „	
„ 80 „	...	1.01 „	
„ 90 „	...	1.06 ₅ „	
„ 100 „	...	0.92 „	
Mean velocity	...	1.094 cc.	

The apparent dissolution velocity had thus increased by not less than 7 per cent. when the barometric pressure had fallen. Experiment 6 was repeated under practically the same barometric pressure as before, with almost identical result. To ascertain the influence of the pressure, Experiment 6 was repeated with the alteration that the apparatus was subjected to a partial vacuum. The results were as follows :—

EXPERIMENT 8.

Weight of wire	...	...	0.2183 grammes
Surface „	...	...	1.99 sq. cm.
Barometric pressure (corr.)	...	...	752.4 mm.

	Volume of hydrogen of 760 mm. and 0° C. evolved per 10 minutes per sq. cm.			Under pressure in mm. mercury.
After 20 minutes	1.64 cc.	...	...	163.0
„ 30 „	1.86 „	...	...	157.5
„ 40 „	1.57 „	...	...	153.0
„ 50 „	1.49 „	...	...	156.0
„ 60 „	1.39 „	...	...	158.5
„ 70 „	1.55 „	...	...	159.0
Average	1.583 cc.			Average 157.8 mm.

The lowering of the pressure from 758.4 mm. in Experiment 6 to 594.6 mm. in Experiment 8 had increased the mean velocity from 1.056 to 1.583, or by more than 50 per cent. It will thus be seen that the pressure influences the dissolution velocity of metals most considerably, and that no conclusion can be drawn from experiments of this kind unless they are carried out under exactly similar conditions. Apart from more exhaustive theoretical deductions, which would fall outside the scope of this paper, I might mention the following general observations :—

1. A binary alloy like Muntz's metal dissolves slowly at first, the velocity then quickly arrives at a maximum, then it falls suddenly, to keep nearly constant for a considerable period, after which a more or less rapid fall occurs. This agrees in most respects with what has been found by other investigators for slightly impure metals in dilute acids.

2. During the period of constant velocity the surface must alter as the resistance capacity, if the action is galvanic. This phenomenon could, however, be more easily treated according to the theory of mass action in heterogeneous systems.

3. There is a distinct indication that the actual mass of the metal in ratio to that of the solvent influences the result. In our case, where 92 cc. of strong acid were used with very small quantities of metal, I invariably got higher results by using smaller quantities of metal, than when a larger quantity was used.

4. The pressure has a very considerable effect on the reaction velocity by influencing the speed with which the hydrogen can leave the surface of the metal.

5. If the action is galvanic, then the seat of the electromotive force is in the electrolyte itself outside the conductor, as the constancy of action indicates a steady E.M.F. of considerable magnitude. Whether the mechanism is one of atomic voltaic combinations between the dissociated ions of the acid, or consists in a delivery of the charges of the hydrogen ions, is immaterial.