CHAPTER V.

INFLUENCE OF TEMPERATURE ON THE PROPERTIES OF ALLOYS.

It frequently happens that metals and alloys are used at temperatures either above or below the normal atmospheric temperature, and it is of considerable importance to know how the metal will behave under these abnormal conditions. The influence of high temperatures is perhaps of greater practical importance than that of low temperatures; but at the same time the results obtained by Dewar, Hadfield, and others at low temperatures are of the greatest value. The available data relating to the subject are not numerous, and in many cases the results are conflicting. Moreover, in some cases the results obtained in actual practice have not been in accordance with those obtained experimentally. The explanation of these discrepancies is probably to be found in the fact that the alteration in the properties of a metal or alloy due to variations in temperature is not always of the same nature, and before dealing with experimental results we may with advantage consider the possible changes which may be brought about in a metal by a variation in temperature.

In the first place, with an increase in temperature and consequent increase in molecular activity, we should expect a gradual and regular falling-off in the tensile strength until, in the neighbourhood of the melting-point, the tenacity becomes *nil*. Moreover, this change should be common to all metals, and experimental proof of it is not lacking. Thus Dewar has shown that at −182° mercury has a tenacity about half that of lead at the ordinary temperature, and iron, copper, nickel, aluminium,

etc., exhibit a marked increase in tensile strength at the same low temperature. The following figures show the tensile strength and elongation of copper at temperatures between −182° and +530°, the first two results being those of Hadfield and Dewar, and the remaining figures those of Le Chatelier. The two results at normal temperature are sufficiently close to justify the figures being regarded as a single series of observations (the small difference being due to the fact that Le Chatelier employed a purer sample of copper and in a completely annealed state), and they may be taken as representing the normal behaviour of a pure metal or a homogeneous solid solution.

MECHANICAL PROPERTIES OF COPPER AT VARYING TEMPERATURES.

Temperature.	Tensile strength. Tons per sq. in.	Elongation.
−182	23	45
+15	15	42
15	14·7	47
110	12·9	41
200	11·4	36
330	9·6	34
430	8·1	17·8
530	4·6	16·4

Normal behaviour, such as that exhibited by copper, is comparatively rare, and we have now to consider abnormal behaviour, which may be due to—

1, An allotropic change in the metal taking place suddenly; 2, a molecular change taking place slowly; 3, a heterogeneous structure.

1. **Allotropic Change.** — Examples of allotropic changes accompanied by changes in the physical properties taking place in metals are not uncommon. Thus iron undergoes a change at 760° and also at 860°, the three varieties of iron being described by Osmond as α iron, existing at temperatures below 760°; β iron, existing between 760 and 860°; and γ iron at temperatures above 860°. α iron is soft and magnetic, β iron is non-magnetic, and γ iron is hard and non-magnetic. Nickel undergoes a change at an even lower temperature, viz. 300°, above which temperature

it ceases to be magnetic. Zinc is brittle at the ordinary temperature, but at 150° it becomes malleable, and again loses this property at higher temperatures. Tin at low temperatures, but not lower than those reached in cold climates, undergoes a molecular change and falls to powder. Such changes are abnormal, and it is not yet known except in the case of iron to what extent these changes may take place in the metals when alloyed.

2. **Gradual Molecular Change.**—Some metals and alloys undergo a gradual change in their crystalline character, which is greatly accentuated as the temperature is raised. The change may be simply an increase in the size of the crystals, or may even be a change in the crystalline form. As an example of the gradual growth of crystals we may take the case of brass containing 70 per cent. of copper, and aluminium bronze containing less than 8 per cent. of aluminium. If these alloys are annealed at comparatively low temperatures the crystals develop in size and there is a marked falling-off in the mechanical properties. This growth of crystal will be referred to later.

3. **Heterogeneous Structure.**—Alloys containing two or more constituents are more liable to suffer deterioration at high temperatures than those containing only one constituent, especially if one of the constituents is a eutectic. The eutectic having a melting-point often very much lower than the constituent metals, is affected at a correspondingly lower temperature; and if the eutectic forms, as is frequently the case, a network or cement round the grains or crystals of the alloy, the strength of the eutectic represents the strength of the alloy. An example of this is found in copper containing bismuth.

Considering these three causes of deterioration it will be seen that one of them, the second, would not occur until after the lapse of some time, and this is sufficient to explain the failure in actual practice of alloys which had given excellent results when merely tested at high temperatures. It is therefore important to note that mechanical tests carried out at high temperatures are not sufficient to indicate the behaviour of the metal in practice.

One of the most important applications of metals and alloys at high temperatures occurs in firebox plates, and more especially firebox stays, and it is in this connection that most of the work on the strength of alloys at high temperatures has been carried

out, and attention has been particularly directed to the alloys of copper. The mechanical requirements of a metal suitable for firebox stays are that it can be easily worked and riveted, and that it shall be as soft as, or softer than, the copper plates into which they are riveted. The alloys examined include bronze, phosphor-bronze, manganese-bronze, aluminium-bronze, brass, copper-nickel alloys, and mild steel. The behaviour of these alloys will be briefly considered. As regards the temperature actually reached by the plates and stays there is a considerable difference of opinion, and it is difficult to arrive at any conclusions from experimental data. Webb has measured the temperature of the centres of a number of firebox stays by drilling a hole through the centre of the head and inserting a thermo-couple. The results showed that at a distance of 2 ins. from the furnace end the temperature varied from 170° to 175° in a boiler working at 120 lbs. pressure, steaming heavily and blowing off, while at a distance of half an inch from the furnace end the temperature rose to 215° to 230° under the same conditions. An attempt to determine the temperature of the surface of the copper plate and of the ends of the stays inside the firebox, in the vicinity of the brick arch, gave temperatures of 540° and 615° respectively. It must be remembered, however, that there is intense local heating, and it is no uncommon thing to see the surface of the copper plate showing drops of copper where the metal has been actually melted. It is difficult, therefore, to say what temperatures are actually reached, but it may be taken that the stays reach a temperature of at least 200°, and probably considerably more.

Bronze.—The only alloys of the copper-tin series available for the purpose of firebox stays are those containing less than 8 per cent. of tin (that is to say, those consisting of a solid solution of tin in copper), and these are probably the least satisfactory of any alloys. Their mechanical properties fall off rapidly at about 200°, a bronze giving a tensile strength of 11 tons per sq. in. at 200° falling to 7·8 tons at 260°.

In an actual test carried out by Webb, the boiler of a six-wheels coupled goods engine working at 150 lbs. per sq. in. was fitted with bronze stays containing 3 per cent. of tin. After running 93,290 miles 145 stays had to be removed as defective, and the average rate of renewal worked out at one stay per 791 miles.

Phosphor-Bronze.—The phosphor-bronzes possessing the mechanical properties suitable for firebox stays are those containing small percentages of tin and only traces of phosphorus. In fact, the phosphorus merely acts as a deoxidiser, and produces a better class of bronze than that obtained by ordinary melting. Data relating to the properties of phosphor-bronze at high temperatures are scarce, but it is probable that they would possess distinct advantages over ordinary bronze.

Aluminium-Bronze.—The alloys of aluminium and copper containing less than 8 per cent. of aluminium possess the required qualities necessary for firebox stays, but they deteriorate very rapidly at high temperatures. A bronze containing 7·1 per cent. of aluminium, which showed a tensile strength of about 25 tons per sq. in. with an elongation of 89 per cent. on 2 ins. at the ordinary temperature, gave only 9 tons per sq. in. and 14 per cent. elongation at 400°.

An actual test carried out by Webb under the same conditions as those described in the case of the copper-tin stays gave disastrous results. The alloy contained 7 per cent. of aluminium, and after being in use only two months and running 2400 miles, the engine had to be taken off the line owing to the number of breakages.

Le Blant also states that the alloys of copper and aluminium are the most sensitive to an increase in temperature, and these practical results are the more remarkable, inasmuch as Charpy describes the aluminium-bronzes as being superior to other copper alloys. The explanation of this discrepancy is to be found in the fact that aluminium-bronze (containing less than 8 per cent. of aluminium) is one of those alloys which undergo a gradual change on heating. At a temperature of 180° (and possibly lower) the crystals increase in size until they reach very large dimensions, and the growth of the crystals is accompanied by a falling-off in the strength of the alloy. Photographs 28, 29, 30 and 31 show the changes which take place in the structure of aluminium-bronze, the alloy represented being the actual material used in Webb's experiments. No. 28 is the original material as supplied. Nos. 29 and 30 represent the same sample after prolonged heating at a low temperature. No. 31 is the same sample heated to a higher temperature, but still below its melting-point. Test

pieces of the alloy showing large crystals, as in photograph 30, give low tensile tests and show a curious crinkling of the surface over the whole length of the specimen.

Brass.—Copper-zinc alloys of varying composition may be used for firebox stays, the percentage of zinc varying from 0 to about 40. Those containing less than 10 per cent. of zinc appear to give fairly good results in practice. Thus, in Webb's experiments, a locomotive boiler working under the same conditions as those previously described, and fitted with stays made of brass containing 90 per cent. of copper and 9 per cent of zinc, gave results equivalent to a renewal of one stay per 5588 miles. The renewals were mostly due to wasted heads and leakage, rather than actual breakage. Alloys containing a higher percentage of zinc but not exceeding about 30 per cent. (that is to say, those consisting of a single solid solution) show a decided falling-off in strength with an increase in temperature.

Brasses containing about 40 per cent. of zinc, consisting of two constituents, both solid solutions, give very poor results. Webb found that an alloy containing 40 per cent. of zinc gave results equivalent to one stay renewed per 262 miles only.

Copper-Nickel Alloys.—Copper containing about 5 per cent. of nickel has been used for firebox stays with good results. The alloy maintains its strength fairly well at high temperatures, and it has been stated that it fulfils all the requirements of a satisfactory and reliable stay material. Unfortunately the results obtained in actual practice are wanting. The alloy is only slightly affected by extremely low temperatures.

Manganese-Bronze.—An alloy consisting of about 96 per cent. copper and 4 per cent. manganese, which is sometimes referred to as cupro-manganese, but sold commercially as manganese-bronze, is now very largely used, both in this country and abroad, for firebox stays. In a report submitted to the Congrès International des Méthodes d'Essais des Matériaux de Construction on locomotive firebox stays, Le Blant states that the metal which he has found least sensitive to heat is cupro-manganese. He concludes: "As the matter stands at present, the metal giving the least number of breakages is cupro-manganese. But it behaves badly under the action of the flames. It ought, therefore, to be reserved for the lines of stays which break most frequently, and as far as

possible from the fire." This suggestion is carried out, and the following results obtained in actual practice, which are due to M. du Bousquet of the Northern Railway of France, are of considerable interest.

Twenty locomotives were fitted with cupro-manganese stays in the upper three horizontal rows of the side plates and the back plate, the remaining stays being copper. Each firebox had 185 cupro-manganese stays and 986 copper stays, and the boiler pressure was 213 lbs. per square inch. In four years only six breakages of cupro-manganese stays occurred, while 1875 copper stays were broken. In spite of the fact, therefore, that the cupro-manganese stays were placed in positions where it was known that breakages were most likely to occur, the breakages of copper stays were 58·6 times as frequent as breakages of cupro-manganese stays. Another set of twenty-five locomotives were fitted entirely with cupro-manganese stays, each firebox containing 1163 stays, and at the end of twelve months only one stay had had to be replaced. In another set of twenty locomotives cupro-manganese stays had been fitted in the upper three rows and in the corners of the side plates, each firebox containing 190 cupro-manganese stays and 973 copper stays. At the end of twelve months' running no cupro-manganese stay had failed, while 232 copper stays had had to be replaced.

Cupro-manganese stays have been used for some years by the Northern Railway of France, the Southern Company of France, and the Hungarian State Railways. The results appear to have been perfectly satisfactory, and the same alloy is now very largely used, but its employment in this country is of more recent date. A cupro-manganese, however, under the name of **crotorite** has been manufactured for some time past by the Manganese Bronze and Brass Company. At very low temperatures (−182°) cupro-manganese shows an increase in tenacity and ductility, and Le Blant's statement that of all the copper alloys cupro-manganese is the least affected by change in temperature appears to be amply justified.

Changes produced in other physical properties of alloys, such as electrical conductivity and magnetism, are considered elsewhere.

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CHAPTER VI.

CORROSION OF ALLOYS.

In spite of the fact that the influence of corrosive liquids on metals and alloys is an important problem in many industries, there is very little available information on the subject. This is probably due partly to a widespread reluctance to publish the results of practical experience, and partly to the difficulties of experimental investigation. It is obvious that experimental tests can seldom reproduce the conditions which obtain in practice, but it is nevertheless possible to obtain comparative results which are of considerable value.

The process of corrosion may take place in several ways. The simplest of these may be described as chemical corrosion—that is to say, the alloy is merely dissolved in the liquid in the same way that a simple metal is dissolved in acid, such as zinc in sulphuric acid.

A more complicated process of corrosion occurs in the combined influence of a corrosive liquid and the atmosphere. This is of very common occurrence, and is frequently observed in the case of copper alloys, the maximum effect of the corrosion taking place at the surface of the liquid or when the metal is alternately immersed in the liquid and exposed to the air. An example of this is seen in the corrosion of brass by salt water. When totally immersed the corrosive action is slow, but in the presence of the atmosphere oxychloride of copper is produced, and rapid corrosion of the brass takes place.

Perhaps the most interesting and the commonest type of corrosion is that which may be described as electro-chemical. This occurs when two bodies possessing different electrical

properties are immersed in contact with one another in a corrosive or conducting liquid. Owing to the difference of potential between the two bodies an electromotive force is set up, or, in other words, a galvanic battery is formed, and one of the bodies passes rapidly into solution. For this reason metals and alloys of different properties must not be placed in contact under liquids. Here we are dealing with two metals or alloys in contact, and the case is comparatively simple; but it follows that the same action will take place in a single alloy if it is not homogeneous in structure. For example, an alloy whose constituents separate out on cooling, or form compounds which separate on cooling, will almost certainly be rapidly corroded on account of the difference of electrical potential between the constituents. Hence alloys forming solid solutions are usually better able to resist corrosion than non-homogeneous alloys. Impurities due to the improper treatment of the alloy, such as dross, slag, oxides, etc., behave in a similar manner. Thus in the case of copper alloys the presence of copper oxide is particularly injurious, and the oxychloride of copper formed by the action of air and sea water on copper alloys accelerates corrosion in the same way. The influence of impurities on corrosion has received more attention in the case of metals than in the case of alloys, and it is well known that many metals in a pure state are only soluble with difficulty in acids, whereas the same metals in an impure state are readily soluble in the same acids.

In some cases the process of corrosion stops itself automatically by the production of compounds which hinder further corrosion. Cases of this description are not uncommon, and an example of the greatest importance occurs in the employment of lead pipes for carrying water. It is well known that lead is appreciably soluble in water, and to such an extent as to render the water unfit for drinking purposes. Moreover, nearly all waters contain considerable quantities of sulphuric acid in the form of sulphates, which also have a corroding action on lead; but the product of the corrosion in this case is a practically insoluble compound, lead sulphate, which forms a coating on the surface of the metal and effectually prevents further corrosion, either by sulphates or by the water itself.

Similar incorrodible coatings are formed on certain alloys, and

an interesting example may be cited to illustrate this and also another protective influence exerted by one metal upon another. This is found in the case of an alloy of gold and silver containing 50 per cent. of each metal, which is practically insoluble in the ordinary acids. In hydrochloric acid or aqua regia a coating of silver chloride is immediately formed, and all action ceases. In nitric acid the silver on the surface is dissolved, and the alloy is then protected by a coating of gold which prevents further action taking place. This fact is well known to all assayers and refiners, and in the operation of "parting" bullion (*i.e.* dissolving out the silver with acid) it is necessary that the amount of silver should be considerably in excess of the gold, or the parting is incomplete. Certain copper alloys behave in a similar manner, the alloying metal being dissolved out until a surface deposit remains, which is only slightly acted upon by the corroding liquid.

The greatest number of experiments on the subject of corrosion appear to have been carried out in connection with the corrosion of metals by sea water, and some of these may be briefly referred to. Milton and Larke, in an interesting paper on the "Decay of Metals," define "decay" as the solution of one constituent only of an alloy as distinguished from "corrosion" by which the metal is attacked as a whole. They confirm the statement that 1 per cent. of tin added to brass and Muntz metal assists them to resist corrosion or decay, and their conclusions are as follows:

"1. Decay is more frequent in metals that have a duplex or more complex structure than in those which are comparatively homogeneous.

"2. Decay is due to slower or less energetic action than that causing corrosion; moreover, it requires an action which removes part only of the constituents of the metal, whereas 'corrosion' removes all the metal attacked.

"3. Both decay and corrosion may result from chemical action alone, or from chemical and electrolytic action combined.

"4. Pitting, or intense local corrosion, is probably often due to local segregation of impurities in the metal; but it may also in some places be due to favourable conditions furnished by local irregularities of surface or structure, producing local irregularities in the distribution of galvanic currents.

"5. For brass exposed to sea water, tin is distinctly preservative, while lead and iron are both injurious, rendering the alloy more readily corrodible. The percentage of the two latter metals, therefore, should be kept as low as possible in all brass intended for purposes where contact with sea water is inevitable.

"6. With a view to obtaining a minimum of corrosion the internal surfaces of condenser tubes should be as smooth and uniform as possible; and in order to ensure this condition, the cast pipe from which they are drawn should be smoothly bored inside, either before the drawing is commenced or in an early stage of the process, as is done in the manufacture of brass boiler tubes.

"7. The experiments with an applied electric current show that electrolytic action alone, even where exceedingly minute currents are employed, may result in severe corrosion or decay. Every effort, therefore, should be made to prevent such action by careful insulation of all electric cables. Where galvanic action is inevitable through the proximity of different metals exposed to the same electrolyte, the currents resulting should be neutralised by the application of zinc plates in the circuit, so arranged that they will be negative to both of the other metals."

Diegel has studied the same subject, and his results may be summarised as follows:—He finds that in brasses containing much zinc the addition of nickel exerts a beneficial influence. This is contrary to the experience of Mr Rhodin (whose work will be considered later), who states that "from a practical point of view nickel is incompatible with low percentage brasses."

The loss in weight in grams per square metre of several alloys suspended for twelve months in sea water is given by Diegel as—

Mild steel . . . . 9·015
Copper-nickel (42 per cent. Ni) . . . 2·162
        ,,   (20 per cent. Ni) . . . 1·848
Copper-aluminium (9 per cent. Al) . . . 0·600

In contact with iron the alloys suffered practically no loss.

As regards the copper-aluminium alloys, Carpenter and Edwards have compared five alloys of copper and aluminium with Muntz metal and naval brass. The alloys were suspended in sea water which was changed every week, and the results, expressed in

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change of weight in pounds per square foot per month, are shown in the following table :—

Alloy.	Composition.	Change in Weight.
2	1·06 per cent. Al.	·0028 lb.
4	2·99 ,, ,,	·0001
6	5·07 ,, ,,	·0000
9	7·35 ,, ,,	·0000
13	9·90 ,, ,,	+ ·0001
Muntz metal	...	– ·0014
Naval brass	...	·0018

The authors explain the gain in weight in the case of the alloy containing 9·9 per cent. of aluminium by supposing that there is a slight oxidation of aluminium on the surface of the alloy. In contact with iron and under the same conditions the alloys were completely protected, while the iron lost ·008 lb. per month. On the other hand, in fresh water and in contact with iron, the aluminium alloys were corroded, while the Muntz metal and naval brass suffered no loss. The actual results were as follows :—

Alloy.	Composition.	Change in Weight.
2	1·06 per cent. Al	·0008
4	2·99 ,, ,,	·0008
6	5·07 ,, ,,	·0008
9	7·35 ,, ,,	·0010
13	9·90 ,, ,,	·0010
Muntz metal	...	·0000
Naval brass	...	·0000

In these experiments the aluminium alloys were from cast samples, while the Muntz metal and naval brass were from rolled samples, so that the results are not strictly comparable.

Manganese-bronze is practically unaffected by sea water, and is in consequence largely used in the manufacture of propellers and propeller blades. Rolled or malleable phosphor-bronze is also little affected by sea water, and has proved satisfactory where brass and steel were useless.

Apart from the corrosive action of sea water there are many important industrial problems connected with the corrosion of metals and alloys. There is a considerable demand, for example, for alloys suitable for the construction of pumps and pumping machinery dealing with corrosive liquids such as acid mine waters, and also for alloys suitable for evaporating pans, stirrers, etc., but,

as already mentioned, there is very little reliable information connected with these subjects. The Bonifacius Coal Mining Company of Westphalia made a series of comparative experiments with wrought iron, steel, and delta metal, which showed very decided advantages in favour of delta metal. Bars $7\frac{1}{2}$ inches long with a sectional area of ·62 inch were immersed in the mine water for $6\frac{1}{2}$ months and the loss in weight determined. The results were as follows :—

	Wrought Iron.	Steel.	Delta Metal.
Weight of original bar .	1·1805	1·2125	1·2787
Weight of corroded bar .	·6393	·6614	1·2633

A series of experiments on the corrosion of copper alloys by acid mine water have also been described by a writer in the *Brass World*. In this case the water contained 12·58 per cent. of free sulphuric acid and 49·90 per cent. as sulphates. The six alloys tested had the following compositions :—

Alloy.	Copper.	Zinc.	Tin.	Lead.	Manganese.	Aluminium.	Iron.
Manganese-bronze, cast	57·20	40·14	1·18	0·02	0·03	0·10	1·33
Manganese-bronze, rolled .	62·45	36·00	0·63	0·06	0·02	...	0·84
Muntz metal, rolled .	57·55	40·02	1·49	0·56	...	...	0·38
Bronze . . .	82·30	...	17·70	...	...	...	...
Red brass .	80·75	1·73	8·73	8·74	...	...	0·05
Hydraulic metal	83·05	6·00	10·81	0·10	...	...	...

The relative losses expressed in weight per cent. were—

Hydraulic metal	.	0·58	Bronze	2·00
Red brass .	.	0·70	Manganese-bronze (rolled) .	4·36
Muntz metal	.	1·83	Manganese-bronze (cast) .	6·37

Unfortunately, in these experiments the samples were of different shapes, and it is obviously misleading to express the results in weight lost without considering the extent of surface subjected to corrosion. Evidently the results require confirmation.

With a view to determining the relative rates of corrosion of

copper alloys in acid liquids the author carried out a series of
tests on the following fourteen commercial copper alloys:—

1. Gun-metal.	8. Cast phosphor-bronze D.
2. Cast gun-metal.	9. Manganese-bronze.
3. Cast brass.	10. Immadium bronze I.
4. Rolled brass.	11. ,, ,, II.
5. Cast phosphor-bronze A.	12. Aluminium-bronze.
6. ,, ,, B.	13. Crotorite.
7. ,, ,, C.	14. Rolled phosphor-bronze.

The liquids selected were sulphuric acid, sulphuric acid contain-
ing sulphate of iron, hydrochloric acid, and hydrochloric acid
containing sodium chloride. The results, which are only
comparative for the series, are given in grams dissolved per
square metre of surface.

Corrosion in a 10 per cent. Solution of Sulphuric Acid.

1. Immadium-bronze I . . .	4·23
2. Rolled phosphor-bronze . .	5·31
3. Aluminium-bronze . .	7·00
4. Cast phosphor-bronze C . .	7·37
5. Rolled brass . . .	7·43
6. Cast brass . . .	7·48
7. Rolled gun-metal . .	7·52
8. Cast gun-metal . . .	8·13
9. Cast phosphor-bronze B . .	8·54
10. ,, ,, D . .	10·56
11. ,, ,, A . .	11·36
12. Crotorite . . .	11·43
13. Immadium-bronze II . .	12·02
14. Manganese-bronze . .	13·83

Corrosion in Sulphuric Acid containing Iron Sulphate.

1. Immadium-bronze I . . .	8·47
2. ,, ,, II . .	12·02
3. Cast phosphor-bronze A .	18·66
4. Crotorite . . .	21·96
5. Rolled phosphor-bronze .	22·51
6. Rolled gun-metal . .	23·06
7. Manganese-bronze . .	23·52
8. Cast phosphor-bronze D .	23·67
9. Rolled brass . .	24·58
10. Cast brass . . .	24·80
11. Cast gun-metal . .	24·91
12. Cast phosphor-bronze C .	25·81
13. ,, ,, B .	27·13
14. Aluminium-bronze . .	29·76

Corrosion in a 20 per cent. Solution of Hydrochloric Acid.

1. Immadium-bronze I . . .	2·12
2. ,, ,, II . .	4·67
3. Rolled brass . . .	5·72
4. Manganese-bronze . .	5·76
5. Rolled phosphor-bronze .	5·95
6. Aluminium-bronze . .	6·13
7. Cast brass . . .	6·69
8. Crotorite . . .	8·46
9. Rolled gun-metal . .	8·72
10. Cast phosphor-bronze A .	9·13
11. Cast gun-metal . .	9·40
12. Cast phosphor-bronze B .	9·61
13. ,, ,, C . .	11·47
14. ,, ,, D . .	16·48

Corrosion in a Solution of 20 per cent. Hydrochloric Acid and 10 per cent. of Sodium Chloride.

1. Immadium-bronze II . .	28·94
2. Rolled brass . . .	31·45
3. Manganese-bronze . .	32·75
4. Immadium-bronze I . .	34·81
5. Cast brass . . .	35·63
6. Aluminium-bronze . .	41·14
7. Crotorite . . .	44·83
8. Cast phosphor-bronze A .	45·44
9. ,, ,, B .	46·56
10. ,, ,, C .	47·11
11. Rolled phosphor-bronze .	48·54
12. Rolled gun-metal . .	48·62
13. Cast gun-metal . .	48·80
14. Cast phosphor-bronze D .	54·52

Mr Rhodin has made a special study of the corrosion of copper
alloys, and he divides alloys into two classes which he describes as
"balanced" and "unbalanced." Balanced alloys are supposed
to be analogous to double salts, and the theory of solution is as
follows:—When brass (to take an example) dissolves in hydro-
chloric acid, zinc chloride and copper chloride are formed. Now
the heat of formation of zinc chloride is greater than that of
copper chloride, hence in order that the total energy of the
system may remain balanced, the "tendency to dissolve would
vary directly as the heats of formation." Further, the zinc
and copper will carry current in the direct ratio of their
conductivities, and dividing by the densities, we have two

expressions representing the ratio of the weights of each metal dissolved.

$$\frac{V \times M \times C}{D},$$

where   V is the valency of the metal,

          M the molecular heat of formation of the chloride,

          C the conductivity,

and   D the density.

In the case of brass, these expressions give values for copper and zinc of 61 and 39 respectively, which is approximately the composition of Muntz metal and the alloy which Mr Rhodin finds the least corrodible of the copper-zinc alloys. In confirmation of
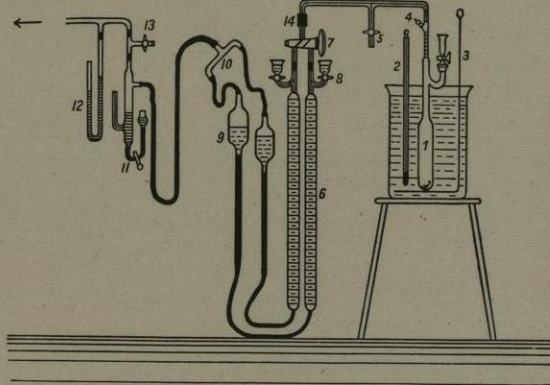

FIG. 26.—Rhodin's Corrosion Apparatus.

this theory Mr Rhodin states that the addition of a more electro-positive metal such as aluminium decreases the solubility of a brass containing 70 per cent. of copper, but increases that of brasses with less than 60 per cent. of copper ; whereas the addition of an electronegative metal such as tin has exactly the reverse effect.

In order to compare the rates of dissolution of alloys Mr Rhodin has devised an apparatus for measuring the volume of hydrogen evolved during a given time. The apparatus is shown in fig. 26, and explains itself.[1] The water-bath in which the dissolution flask is immersed must be kept at exactly the same temperature, and two burettes are provided with a three-way cock, so that readings can be taken at intervals of ten minutes by using

[1] Figs. 26 and 27 are inserted by permission of publishers of *Engineer*.

the burettes alternately. The alloy to be tested is drawn into wire about 0·5 mm. in diameter, and a length is cut off sufficient to provide a surface of 2 sq. cm. Strong hydrochloric acid is used as a solvent, and for copper alloys a temperature of 80° is maintained. Fig. 27 represents some curves given by Mr Rhodin as typical of the following alloys :—
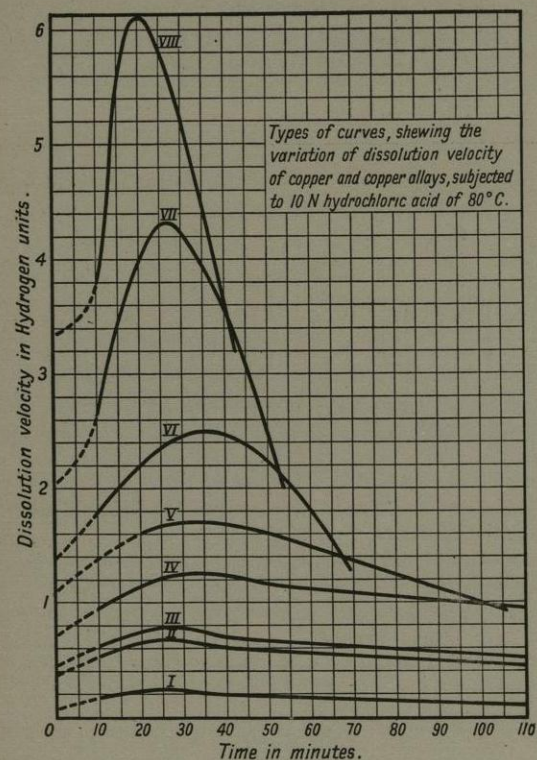

FIG. 27.—Rhodin's Typical Curves.

    I. Copper of good quality.

   II. Bronze containing 90 per cent. copper and 10 per cent. Sn.

 III. Admiralty gun-metal.

  IV. Muntz metal and very good manganese-bronze.

   V. Brass containing 70 per cent of copper.

  VI. Low percentage brasses, rich in iron.

VII. and VIII. Low percentage brasses of manganese-bronze type which contain incompatible ingredients.

As the result of his experiments Mr Rhodin arrives at the conclusion that in a given series of copper alloys "the alloy which has the flattest and most regular dissolution curve does at the same time possess the best mechanical properties."

As regards the corrosion of steel and iron alloys Howe has made a number of exhaustive trials with wrought iron, steel and nickel steel. The plates tested in these experiments weighed 2597 lbs., and the total area exposed was 928 sq. ft. The results are summed up in the following table, wrought iron being taken as the standard in each case :—

	Sea Water.	Fresh Water.	Atmosphere.	Average.
Wrought iron . .	100	100	100	100
Mild steel . .	114	94	103	103
3 per cent. nickel steel .	83	80	67	77
26 per cent. nickel steel .	32	32	30	31

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CHAPTER VII.

COPPER ALLOYS, BRONZE.

It is customary to consider the alloys of copper under three heads, viz. (1) The bronzes, or alloys consisting mainly of copper and tin ; (2) the brasses, consisting mainly of copper and zinc ; and (3) other alloys of copper. Although not an entirely satisfactory classification, there is much to be said in its favour, and it is to be regretted that manufacturers in some instances use the terms brass and bronze indiscriminately. Alloys, for example, containing from 60 to 70 per cent. of copper and 30 to 40 per cent. of zinc, together with small percentages of iron, aluminium, or manganese, would be far more accurately described as brasses than bronzes, and yet these alloys are frequently described and sold as bronzes. If such alloys contain aluminium or manganese, or even if these metals have been employed in their manufacture, they might be described as aluminium-brasses or manganese-brasses, but not bronzes. The terms brass and bronze are so firmly established in the English language that it would be impossible (even if desirable) to adopt any other classification, and the words should therefore be employed with discretion.

Bronze.

Historical.—The word *bronze*, derived from the Italian *bronzo*, appears to have been introduced into the English language in the 16th century. The alloy, however, was known in very early times, and a rod of metal found by Dr Flinders Petrie at Meydum, and estimated to belong to a period about 3700 B.C., was found to contain 89·8 per cent. of copper and 9·1 per cent. of tin,