

XLI.—*Action of Acids upon Metals and Alloys.*

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It has frequently occurred to us, in the course of our investigations into the physical properties of metals and alloys, that it would be interesting both in a scientific and practical point of view, if we were carefully to examine the action of some of the acids upon them. We, therefore, submitted copper, zinc, and tin, and the two classes of alloys which are obtained from these metals, viz., brasses and bronzes, to the action of sulphuric, nitric, and hydrochloric acids.

In this series of researches we have followed the same plan as when we experimented upon the "conductibility," the "specific gravity," &c., &c. of metals and alloys; viz., we first examined the action of these acids upon the pure metals, and afterwards upon the alloys composed of the pure metals melted together in equivalent and multiple proportions.

Our experiments having been very numerous, and therefore, having extended over a long period of time, we have deemed it advisable to divide our paper into two parts.

First—The action of sulphuric acid upon zinc, copper, and tin, and of nitric and hydrochloric acids on the same metals.

Secondly—The action of the same acids upon their alloys, viz., brasses and bronzes.

*On the marked influence which an Oxidized Surface has on the subsequent action of Sulphuric Acid of various strengths on Zinc.*

Before entering into the details of our experiments, it is necessary that we should state, that it was only after considerable time and experience that we were able to determine the exact conditions under which we were to operate, if we wished to obtain constant and correlated results, owing not only to the extreme difficulty attending the preparation of perfectly pure sulphuric acid and a few ounces of pure zinc, but especially to the irregularity of the action of sulphuric acid on zinc, depending, as we observed, upon the peculiar state of its surface. Thus we found that cubes which had been made of the same zinc, but at different times, were acted upon more or less by the same acid when placed under the same circumstances; and these observations gradually led us to the discovery of a curious fact, viz., that a perfectly clean surface of zinc will become, after a few days, sufficiently oxidized by contact with air to modify in a very marked degree the action of sulphuric acid upon it. Thus, if a cube of zinc recently filed is placed in sulphuric acid diluted with 9 eq. water, the action may be considered as null; whilst if the same cube be gently heated in contact with the air and allowed to cool, and be then placed in the same strength of acid, the attack is 10 times greater, as proved by these results.

TABLE.

Quantity of acid . . . . .	50 cent. cube.
Surface of zinc acted on . . . . .	1 „
Time of action . . . . .	2 hours.

STRENGTH OF ACID USED.

Quantity of zinc dissolved.		
SO <sub>3</sub> ,9HO . . . . .	.31	{ Used a clean file carefully kept free from grease to clean surfaces of cube. After filing washed with alcohol to remove grease. After filing heated in gas flame—allowed to cool before using—surface oxidized.
SO <sub>3</sub> ,9HO . . . . .	.03	
SO <sub>3</sub> ,9HO . . . . .	3 .08	

*On the Action of Sulphuric Acid of various Strengths on Zinc.*

In looking over the table following these remarks, and containing our results on the action of various strengths of sulphuric

acid on pure zinc with an unoxidised surface, it will be observed, firstly, that they are contrary to the general view entertained by chemists of the action of sulphuric acid upon that metal, for this acid has no action at ordinary temperatures on zinc; also that it requires a temperature of  $130^{\circ}$  C. before concentrated acid begins to show any marked action, and that it is only at  $150^{\circ}$  C. that the action of sulphuric acid with 1 and 2 equivalents of water, is fully developed. Secondly, on perusing our results, the following curious facts will be observed, viz., that mono- and bi-hydrated sulphuric acids exercise a comparatively limited action on zinc at a temperature of  $130^{\circ}$  C. as compared with that of the tri-hydrated acid; thus, whilst  $\text{SO}_3, \text{HO}$  and  $\text{SO}_3, 2\text{HO}$  will dissolve only respectively 125 or 236.6 grammes zinc on a square metre surface,  $\text{SO}_3, 3\text{HO}$  will in the same space of time dissolve 9860 grammes or 7 to 8 times the amount. Further, the same extraordinary difference of action of these various strengths of acids is maintained when their temperature is raised to  $150^{\circ}$  C.

A similar difference of action is observed when the action of diluted sulphuric acids on the unoxidized surface of pure zinc is studied; thus when  $\text{SO}_3, 6\text{HO}$  acts upon such a metal, only 561.6 grammes per metre surface are dissolved in two hours, whilst  $\text{SO}_3, 7\text{HO}$  dissolves in the same space of time as much as 5260.8 grammes, but in this case the temperature employed was only  $100^{\circ}$  C., or that of the boiling point of the latter acid.

The reactions of sulphuric acid of different strengths upon an unoxidized surface of pure zinc, are far more complicated and interesting than chemists admit. To understand them it is necessary that they should be classed under two distinct heads, viz., the action of  $\text{SO}_3, \text{HO}$ , in which case the metal is oxidized solely at the expense of the acid, sulphurous acid being produced, whilst with  $\text{SO}_3, 2\text{HO}$ , and especially with  $\text{SO}_3, 3\text{HO}$ , not only is sulphurous acid given off, but also simultaneously with it sulphuretted hydrogen.

It is interesting to observe two distinct chemical reactions taking place simultaneously; thus we have an action similar to that which sulphuric acid exercises on the metals of the alkalis or alkaline earths, giving rise to hydrogen and a sulphate of the metal, and that which sulphuric acid has, viz., on the fifth group, etc., viz., mercury, generating sulphurous acid and a sulphate of the metal.

Lastly, it will be observed on looking over the table that sul-

phurous acid gradually disappears, whilst the quantity of sulphuretted hydrogen increases, until in its turn it also disappears and is replaced by pure hydrogen.

TABLE 1.

*Action of Sulphuric Acid of different strengths upon pure Zinc.*

Quantity of acid ..... 50 cent. cubes.  
 Surface acted on ..... 1 " "  
 Time of action ..... 2 hours.

Strength of acid.	Temperature degs. cels.	1 centimetre cube.	1 sq. metre.	Remarks.
SO <sub>3</sub> HO ..	Ordinary	"	"	SO <sub>2</sub> evolved.
" " ..	130°	·075	125·0	SO <sub>2</sub> evolved. No HS.
" " ..	150°	·232	386·6	
SO <sub>3</sub> 2HO ..	Ordinary	·002	3·3	
" " ..	130°	·142	236·6	SO <sub>2</sub> evolved. A little HS.
" " ..	150°	·345	575·0	HS given off and SO <sub>2</sub> .
SO <sub>3</sub> 3HO ..	Ordinary	·002	3·3	
" " ..	130°	5·916	9860·0	Large quantity of HS. A trace of SO <sub>2</sub> . Violent action. Large quantity of ZnOSO <sub>3</sub> undissolved. Same action as above.
" " ..	130°	4·916	8193·3	
" " ..	150°	5·450	9083·3	
SO <sub>3</sub> 4HO ..	Ordinary	·005	8·3	
" " ..	130°	3·080	5133·3	Large quantity of HS given off, with a little SO <sub>2</sub> . Violent action. Quantity of ZnOSO <sub>3</sub> not dissolved.
" " ..	130°	2·389	4731·6	
SO <sub>3</sub> 5HO ..	Ordinary	·049	81·66	
" " ..	130°	·456	760·0	Acid nearly boiling. HS given off. Trace of SO <sub>2</sub> .
SO <sub>3</sub> 6HO ..	Ordinary	·027	45·0	
" " ..	130°	·337	561·6	Boiling point of this acid. HS evolved.
SO <sub>3</sub> 7HO ..	Ordinary	·018	33·0	
" " ..	100°	3·161	5268·3	Violent action at first; after about 20 minutes stopp'd. ZnO, SO <sub>3</sub> undissolved. Surface apparently coated, with no HS. Trace of SO <sub>2</sub> . Attack irregular.
" " ..	"	3·800	6333·3	
" " ..	"	3·060	5100·0	
SO <sub>3</sub> 8HO ..	Ordinary	·035	58·3	
SO <sub>3</sub> 9HO ..	Ordinary	·005	8·3	
SO <sub>3</sub> 10HO	Ordinary	·033	55·3	

*Action of Sulphuric Acid on Copper.*

The following is the action of 50 cubic centimetres of sulphuric acid, of different strengths, upon 1 cent. cube of pure copper, during a period of two hours, and at the temperature of 130° and 150° C.

TABLE 2.

*Action of Sulphuric Acid of different strengths upon pure Copper.*

Surface acted upon.....	1 cent. cube.
Quantity of acid.....	50 " "
Time of action.....	2 hours.
Temperature.....	130° and 150° C.

Sulphuric acid employed.	Temperature degs. cels.	Loss by 1 cent. cube.	Calculated on 1 sq. metre.	Remarks.
SO <sub>3</sub> HO ....	130°	·854	1423·3	Surface of cubes covered with CuS; SO <sub>2</sub> was also evolved.
" " ....	"	·704	1173·3	
" " ....	150°	1·678	2796·7	There was also a residue insoluble in the acid, and composed principally of CuS and CuO,SO <sub>3</sub> . Very slight action.
SO <sub>3</sub> 2HO ....	130°	·008	13·3	
" " ....	150°	·063	105·0	
SO <sub>3</sub> 3HO ....	130°	·004	6·6	
" " ....	150°	·006	9·9	
SO <sub>3</sub> 4HO ....	150°	·000		

These results suggest to us the following remarks: that the temperature at which copper is first attacked by sulphuric acid, SO<sub>3</sub>HO, is 130° C., and that even at a few degrees below that temperature, copper is not acted upon; further, that at 150° C., the quantity of copper dissolved by this acid under the same circumstances is nearly the double of that which SO<sub>3</sub>2HO, SO<sub>3</sub>3HO could dissolve, whilst SO<sub>3</sub>4HO, have little or no action upon that metal.

We further noticed, that the decomposition of SO<sub>3</sub>HO, by copper is far more complicated than it is generally admitted to be; for the action does not consist simply in the decomposition of the acid into oxygen which oxidizes the copper, and sulphurous acid which escapes, but the affinity of copper for oxygen is such that the whole of this gas is removed from a certain portion of the sulphuric acid, leaving free sulphur, which combines with the copper to form sulphide of copper. The reason which leads us to believe that the formation of this compound is due to the direct combination of the sulphur with the copper, and not, as in the case of zinc, to two chemical actions taking place simultaneously, is that if water were decomposed into its constituent elements, its oxygen uniting with the copper, whilst its hydrogen would com-

bine with the sulphur of the reduced sulphuric acid to form sulphuretted hydrogen, which in its turn would act upon oxide of copper to produce the sulphuret of copper, some sulphuretted hydrogen would undoubtedly have been given off, and under the influence of heat, must have escaped, and have been easily detected. Another proof that sulphuric acid is decomposed into oxygen and sulphur, and that water does not participate in the chemical action which ensues is, that free sulphur volatilizes and condenses in the neck of the small balloons employed, which, in our experiments, were placed in an oil-bath maintained carefully at the required temperature. This remarkable reduction of sulphuric acid by a metal is further corroborated by the action of sulphuric acid upon tin, in which case sulphur is also liberated in considerable quantity, but no sulphide of tin produced, owing, probably, to the fact that sulphur has less affinity for tin than for copper.

TABLE 3.

*Action of Sulphuric Acid of different strengths upon Tin.*

Sulphuric acid employed.	Temperature degs. cels.	Loss by 1 cent. cube.	Calculated on 1 sq. metre.	Remarks.
SO <sub>3</sub> HO . . . . .	150°	3·010	5016·6	A large quantity of SO <sub>2</sub> given off. No HS. No SSn, but some free sulphur.
SO <sub>3</sub> 2HO . . . . .	150°	·640	1066·6	SO <sub>2</sub> given off. No HS.
SO <sub>3</sub> 3HO . . . . .	150°	·470	783·3	SO <sub>2</sub> given off and a little HS.
SO <sub>3</sub> 4HO . . . . .	130°	·215	358·3	A large quantity of HS given off with a little SO <sub>2</sub> .
SO <sub>3</sub> 5HO . . . . .	130°	·140	233·3	Acid nearly on the foil. HS given off, and only a little SO <sub>2</sub> .

It will be observed, in examining the results contained in this table, that the action of various strengths of sulphuric acid upon tin, differs entirely from that which they exert upon copper, and in some respects on zinc; SO<sub>3</sub>HO exerts the maximum action upon copper, but it gradually decreases as the acid becomes more diluted; whilst with zinc, as before stated, the action is completely different

according to the strength of acid ; but there is still this similitude between the action of sulphuric acid upon tin and zinc, viz., that with a certain strength of acid, sulphurous acid and sulphuretted hydrogen are given off simultaneously ; but this action does not take place with  $\text{SO}_3, \text{HO}$  or  $\text{SO}_3, 2\text{HO}$ , as the first indication of sulphuretted hydrogen occurs with  $\text{SO}_3, 3\text{HO}$ , and it is only with  $\text{SO}_3, 5\text{HO}$  that large quantities of sulphuretted hydrogen are given off, and only a trace of sulphurous acid. From these results we conclude that when strong sulphuric acid acts upon tin, the metal is oxidized, like on copper, through the action of the acid, whilst with weaker acids water is decomposed, the oxygen fixing itself on the tin or zinc, whilst the hydrogen unites with the sulphur to produce sulphuretted hydrogen ; therefore, the action of dilute sulphuric acid upon tin may be considered as two chemical actions occurring simultaneously ; moreover sulphate of binoxide of tin is produced and not the corresponding salt of protoxide.

The action of sulphuric acid upon tin throws much light on the formation of sulphide of copper, for in the case of tin, as there is no intense affinity between sulphur and that metal, we observe the production of a large quantity of sulphurous acid, no sulphuretted hydrogen, but a large quantity of free sulphur floating in the liquid, showing a complete deoxidation of the sulphuric acid by both metals ; but with this difference, that in the case of tin, sulphur remains free, whilst in that of copper, it combines with it, producing a sulphuret.

*Action of Nitric and Hydrochloric Acids on Tin, Zinc, and Copper.*

—We shall reserve details of our experiments until we describe the results obtained by acting with the same acids on the two classes of alloys formed by these metals, viz., brasses and bronzes ; for it was found by direct experiment that to arrive at any correct data, it was necessary to employ acids of peculiar strength, or otherwise the reactions were so complicated that no comparative results could be obtained of the action of these acids on the various groups of alloys. The following facts will, we believe, illustrate these statements :—

TABLE 4.

*Action of Nitric Acid upon an Alloy of Copper and Zinc.*

Surface acted upon.....	1 cent. cube.
Quantity of acid.....	100 „
Time of action.....	24 hours.
Composition of Brass	{ 1 eq. copper.... 49·059
	{ 1 eq. zinc..... 50·941
	100·000

Strength of nitric acid employed.	Total quantity dissolved on 1 c.c.	Composed of	Per cent.	Average per cent.
Strong acid.	Sp. gr. 1·14	3·093 Cu	48·232 Cu	} 48·258 Cu 51·742 Zn 0·000
		3·328 Zn	51·768 Zn	
	<u>6·421</u>	<u>100·000</u>		
	1·14	3·936	1·898 Cu	
		2·038 Zn	51·717 Zn	
		<u>3·936</u>	<u>100·000</u>	
Weak acid.	1·08	0·252 Cu	16·856 Cu	} 16·741 Cu 83·259 Zn 100·000
		1·243 Zn	83·144 Zn	
	<u>1·495</u>	<u>100·000</u>		
	1·08	2·034	0·340 Cu	
		1·705 Zn	83·374 Zn	
		<u>2·045</u>	<u>100·000</u>	

In perusing the above table, it will be seen that whilst nitric acid of sp. gr. 1·14 dissolves the metals composing the brass in the exact proportions in which they exist in the alloy employed, whilst an acid of about half the strength, or of sp. gr. 1·08, dissolves nearly the whole of the zinc contained in the alloy, and only a small quantity of copper. This result, among others, showed us the necessity of employing a given strength of acid in order to conduct a series of comparative experiments on various alloys, and we consider the action of nitric acid of sp. gr. 1·14 a normal action, as it attacks both zinc and copper in the proportions in which they exist in the alloy, whilst that of a stronger or weaker



acid is abnormal, as it acts according to its strength, more or less, on each of the metals composing a brass alloy. These results were further confirmed by a cube of an alloy composed of equal parts of zinc and copper, being left for several days in hydrochloric acid of full strength, the whole of the zinc, or nearly so, of the alloy, being dissolved, leaving a cube which had the same diameter as if it had only been experimented upon, and was composed of nearly pure copper.

The following table illustrates this fact:—

TABLE 5.

*Action of Strong Hydrochloric Acid on the Alloy ZnCu.*

1 eq. copper .....	49·059
1 eq. zinc.....	50·941
	100·000

Strength of acid used.	Weight of cube.	Amount of zinc dissolved 1 c.c.	Amount of Zn left in cube.	Remarks.
	grammes.	grammes.	grammes.	
1·20	Cu 4·409 Zn 4·577 — 8·986	4·448	·130	The cubes, after the experiment, have copper-like colour, and have the same diameter as before, but are quite soft. A trace only of copper dissolved.
1·20	Cu 4·467 Zn 4·638 — 9·105	4·330	·308	

*Action of weak Nitric Acid on Brasses.*

We shall now proceed to describe the action of weak nitric acid sp. gr. 1·100 on various alloys of zinc and copper, combined in equivalent and multiple proportions. We decided to use this strength of acid, as we found, after many experiments, that this was the best strength of acid that could be employed to obtain constant results.

The table which follows these remarks contains a summary of our results, and gives an idea how varied is the action of the same strength of nitric acid on the same class of alloys, and what an extraordinary influence a few per cent. of copper or zinc, more or less, exerts in preventing or promoting the action of this acid.

Further, in perusing the table, it will be observed that the action of the acid is comparatively violent on all the alloys containing an excess of zinc, and that it is nearly 1,000 times less active on all those in which there is an excess of copper; and we cannot in this case refrain from drawing special attention to the action of the acid on the alloy ZnCu, as compared with that which it exerts upon Zn<sub>2</sub>Cu, although there is only a difference of 17 % of zinc.

It is necessary that we should explain how we have arrived at the data found in the fourth column. The figures represent the calculated results of the amount of metals which should have been dissolved had the metals been free, and had not the presence of one of the metals interfered with the chemical action. It will be observed, in comparing these figures with those which represent the quantity of alloy actually dissolved, that in the first four alloys of the table, viz., those which contain an excess of zinc, the quantity of alloy dissolved is in excess of that which theory indicates, whilst in the alloy composed of equivalents of each metal, and those which contain an excess of copper, the action is 40 or 50 times less. These facts appear to us not only interesting in a scientific point of view, but important in their applications to manufactures, especially for brass taps, pipes, &c.

The following is a summary of our experiments:—

TABLE 6.

*Action of Nitric Acid, sp. gr. 1.100, on Alloys of Copper and Zinc (Brasses).*

Surface acted upon.....	1 cent. cube.
Quantity of acid.....	25 „ „
Time of action.....	15 minutes.
Temperature .....	20° C.

Metals and composition of alloys.	Loss by 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to the composition of the alloys.
Copper	0.009	15.000	15.000
Zinc	1.760	2933.3	2933.3
Zn <sub>2</sub> Cu			
Zn 83.70	2.025	3375.0	2457.645
Cu 16.30			
100.00			

TABLE 6—Continued.

Metals and composition of alloys.	Loss on 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to the composition of the alloys.
$Zn_3Cu$			
Zn 80.43	1.740	2900.0	2362.2
Cu 19.57			
<u>100.00</u>			
$Zn^3Cu$			
Zn 75.36	1.695	2825.0	2214.25
Cu 24.64			
<u>100.00</u>			
$Zn_2Cu$			
Zn 67.26	1.530	2550.0	1977.8
Cu 32.74			
<u>100.00</u>			
$ZnCu$			
Zn 50.95	0.027	45.000	1494.0
Cu 49.05			
<u>100.00</u>			
$ZnCu_2$			
Zn 33.94	0.015	25.000	1005.48
Cu 66.06			
<u>100.00</u>			
$ZnCu_3$			
Zn 25.52	0.013	21.66	759.75
Cu 74.48			
<u>100.00</u>			
$ZnCu_4$			
Zn 20.44	0.015	25.00	611.50
Cu 79.56			
<u>100.00</u>			
$ZnCu_5$			
Zn 17.05	0.010	16.66	512.57
Cu 82.95			
<u>100.00</u>			

*Action of Hydrochloric Acid, sp. gr. 1.05 on Alloys of Zinc and Copper (Brasses).*

It will be observed, in perusing the results consigned in the table following, that the action of this acid is nearly equal to that which theory indicates on the alloys  $Zn_5Cu$  and  $Zn_4Cu$ , whilst in the next alloy,  $Zn_3Cu$ , which contains only 5 % more copper than the preceding one, the attack is only half of that indicated by theory. But certainly the most unexpected result arrived at, is the complete inaction of hydrochloric acid upon all the alloys containing an excess of copper, and especially on the alloy composed of equivalent proportions of each metal; and it is very remarkable that whilst half the cube of the alloy  $Zn_5Cu$  is dissolved in the space of one hour, the alloy with equal equivalents of each of the metals remains perfectly unattacked.

The fourth column in this table also gives the theoretical quantity that should have been dissolved if the metals had been free, and not alloyed.

TABLE 7.

Surface acted upon .....	1 centimetre cube.
Quantity of acid.....	50 " "
Time of action .....	1 hour.

Metals and composition of alloys.	Loss on 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to the composition of the alloys.
Copper	0.000	0.000	0.000
Zinc	0.200	333.33	333.33
$Zn_5Cu$			
Zn 83.70	0.155	258.334	279.00
Cu 16.30			
<u>100.00</u>			
$Zn_4Cu$			
Zn 80.43	0.155	258.334	268.0
Cu 19.57			
<u>100.00</u>			
$Zn_3Cu$			
Zn 75.36	0.065	108.334	251.2
Cu 24.64			
<u>100.00</u>			

TABLE 7—Continued.

Metals and composition of alloys.	Loss on 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to the composition of the alloys.
Zn <sub>2</sub> Cu Zn 67.26 Cu 32.74 <hr/> <u>100.00</u>	0.050	83.334	224.2
ZnCu Zn 50.68 Cu 49.32 <hr/> <u>100.00</u>	0.000	0.000	168.933
ZnCu <sub>2</sub> Zn 33.94 Cu 66.06 <hr/> <u>100.00</u>	0.000	0.000	113.133
ZnCu <sub>3</sub> Zn 25.52 Cu 74.48 <hr/> <u>100.00</u>	0.000	0.000	85.066
ZnCu <sub>4</sub> Zn 20.44 Cu 79.56 <hr/> <u>100.00</u>	0.000	0.000	68.133
ZnCu <sub>5</sub> Zn 17.05 Cu 82.95 <hr/> <u>100.00</u>	0.000	0.000	56.83

*Action of Sulphuric Acids SO<sub>3</sub>HO and SO<sub>3</sub>3HO on Alloys of Copper and Zinc.*

We now pass on to the action exerted by the two above mentioned strengths of sulphuric acid upon brasses, the results of which are not less instructive than those already referred to. But before drawing attention to the leading facts observed, it is necessary that we should give the reason why we employed in preference SO<sub>3</sub>,HO and SO<sub>3</sub>,3HO for our experiments. They are that SO<sub>3</sub>,HO is the only acid which attacks copper, in any marked degree; SO<sub>3</sub>,3HO, the only one which has a corres-

ponding action upon zinc, and therefore by employing these successively upon the same alloy at a temperature of 150° C., we were acting under favourable circumstances for appreciating the exact mode of action of these acids on both metals entering into the composition of the alloy.

TABLE 8.

*Action of Monohydrated Sulphuric Acid on Brasses.*

Surface acted upon .....	1 cent. cube.
Quantity of acid employed .....	50 „
Time of action .....	2 hours.
Temperature.....	150° C.
	0 sq. metre.
Action on 1 c. c. of copper .....	1·678 = 2797
„ „ 1 „ zinc .....	·232 = 3367

Composition of alloys.	Loss on 1 c. c.	Calculated loss 1 sq. metre on surface.	Theoretical loss.	Remarks.
CuZn <sub>3</sub> 83·7 Zn 16·3 Cu				} SO <sub>2</sub> given off. No HS, and only Zn dissolved.
<u>100·0</u>	·098	163·33	779·5	
CuZn <sub>4</sub> 80·43 Zn 19·57 Cu				} SO <sub>2</sub> given off. No HS, and only Zn dissolved.
<u>100·00</u>	·074	123·33	858·3	
CuZn <sub>3</sub> 75·36 Zn 24·64 Cu				} SO <sub>2</sub> given off. No HS, and only Zn dissolved.
<u>100·00</u>	·180	300·0	980·5	
CuZn <sub>2</sub> 67·26 Zn 32·74 Cu				} SO given off.
<u>100·00</u>	·083	183·3	1175·8	
CuZn 50·68 Zn 49·32 Cu				} SO, given off. No HS. Strong action. Insoluble residue consists of ZnO, SO <sub>2</sub> , CuO, SO <sub>3</sub> . Also a small quantity of CuS and S. The quantities of the metals dissolved were found to be in the exact proportion of those in the alloys.
<u>100·00</u>	1 297	2161·6	1375·7	

TABLE 8—Continued.

Composition of alloys.	Loss on 1 c. c.	Calculated loss 1 sq. metre on surface.	Theoretical loss.	Remarks.
$\text{Cu}_3\text{Zn}$ 33·94 Zn 66·06 Cu <hr/> 100·00	1·292	2158·3	2015·0	} $\text{SO}_2$ given off. No HS. A small quantity of free S and CuS.
$\text{Cu}_3\text{Zn}$ 25·52 Zn 74·48 Cu <hr/> 100·00	1·747	2211·66	2182·01	
$\text{Cu}_4\text{Zn}$ 20·44 Zn 79·56 Cu <hr/> 100·00	1·328	2213·0	2304·47	Ditto
$\text{Cu}_7\text{Zn}$ 17·05 Zn 82·95 Cu	·605	1008·33	2386·19	Ditto

In examining the results contained in this table, several interesting data are brought out, viz., that in all the alloys in which there is an excess of zinc over the quantity of copper, the attack is exceedingly limited, whilst in all those in which there is an excess of copper, the action is most marked, and very similar, in fact, to that which acid exerts on pure copper.

It is certainly interesting to observe the extraordinary preventive influence which a metal like zinc has on the action of such a powerful acid as  $\text{SO}_3, \text{HO}$  on copper; and certainly, *a priori*, such a result could have been expected. And we cannot help drawing attention to the striking difference between the action of  $\text{SO}_3, \text{HO}$  on the alloys  $\text{ZnCu}$  and  $\text{Zn}_2\text{Cu}$ , and, therefore, the influence which only 17 % of zinc exercises in preventing the action of the acid, the action on  $\text{ZnCu}$  being nearly 15 times as violent as on  $\text{Zn}_2\text{Cu}$ .

It may be further observed that when  $\text{SO}_3, \text{HO}$  acts upon the above alloys, in all those containing an excess of zinc, not only does the zinc prevent the action of the acid upon

the alloy itself, but it so thoroughly preserves the copper from the action of the acid, that whatever may be the amount dissolved, it is represented by zinc only; whilst in the alloys containing an excess of copper, the copper is attacked also, and dissolved in large quantities. As to the general result of the chemical action of  $\text{SO}_3, \text{HO}$  on the same group of alloys, we may add that the secondary products are the same as when  $\text{SO}_3, \text{HO}$  acts upon copper itself.

*Action of  $\text{SO}_3, \text{HO}$  on Brasses.*

It will be seen, in perusing the results contained in the table which follows these remarks, how very different is the action of  $\text{SO}_3, 3\text{HO}$  as compared with  $\text{SO}_3, \text{HO}$  on the same alloys when placed under identical circumstances, for all the alloys which contain an excess of zinc are those most attacked, whilst this strength of sulphuric ( $\text{SO}_3, 3\text{HO}$ ) acid exerts little or no action upon the alloys containing an excess of copper; and what enhances the value of these results is, that all the alloys which contain an excess of either copper or zinc are attacked more or less, whilst the alloy  $\text{CuZn}$  is not acted on, and therefore this alloy could be employed with marked advantages for many purposes, the more so that when well prepared it has a fine and rich brass appearance, notwithstanding the large proportion of zinc; it contains about 15 % more than the poorest brass alloys usually found in commerce.

Lastly, it will be observed, that among the secondary products formed during the chemical action of  $\text{SO}_3, 3\text{HO}$ , there is no sulphide of zinc produced, as in the case when  $\text{SO}_3, \text{HO}$  acts upon the same alloys of zinc and copper.

TABLE 9.

Surface acted upon .....	1 centimetre cube
Quantity of acid .....	50 " "
Time of action .....	2 hours
Temperature .....	150° C.
	on sq. metre of surface.
Action on 1 c. c. of copper .....	·006 = 10·000
"    "    1    "    zinc .....	5·450 = 9085·150



TABLE 9—Continued.

Composition of alloys.	Loss on 1 c. c.	Calculated on 1 sq. metre.	Theoretical quantity.	Remarks.
CuZn <sub>5</sub> .....	·135	225·0	7605·73	SO <sub>2</sub> given off. No HS. deposits. CuS.
CuZn <sub>4</sub> .....	·130	216·0	7308·95	Ditto. A trace of HS.
CuZn <sub>3</sub> .....	·120	200·0	6848·86	Ditto
CuZn <sub>2</sub> .....	·115	191·6	6113·77	Ditto
CuZn .....	·000	—	4609·2	—
Cu <sub>2</sub> Zn .....	·119	198·33	3090·05	SO <sub>2</sub> given off.
Cu <sub>3</sub> Zn .....	·006	10·0	2325·95	Ditto
Cu <sub>4</sub> Zn .....	·007	11·6	1864·95	Ditto
Cu <sub>5</sub> Zn .....	·006	10·0	1557·29	Ditto

*Action of Acids on Bronzes, or Alloys of Copper and Tin.*

We shall follow the same order in examining the action of various acids upon bronzes as we have done in describing their action upon brasses; thus we shall first examine the action of nitric acid, then that of hydrochloric acid, and, finally, that of sulphuric acids; and it is easy to conceive that the action of these various acids upon bronze alloys must be very different, *nitric acid* possessing the property of acting upon both metals, *hydrochloric acid* of acting only upon tin and not upon copper, whilst *sulphuric acid* only acts upon both metals, but under the influence of heat.

We shall now proceed to examine the action of each acid separately.

TABLE 10.

*Action of Nitric Acid, sp. gr. 1·25, on Alloys of Copper and Tin (Bronzes).*

Surface acted upon ..... 1 cent. cube  
 Quantity of acid ..... 25 „  
 Time of action ..... 15 minutes

Metals and composition of alloys.	Loss on 1 c.c.	Calculated on 1sq. metre.	Calculated loss according to the composition of the alloys.
Copper.....	1·920	3200·0	3200·0
Tin.....	0·505	841·667	841·667
Sn <sub>5</sub> Cu			
Sn .. 90·27			
Cu .. 9·73			
100·00	1·130	1883·33	1071·132

TABLE 10—Continued.

Metals and composition of alloys.	Loss on 1 c.c.	Calculated on 1 sq. metre.	Calculated loss according to the composition of the alloys.
$\text{Sn}_4\text{Cu}$ Sn .. 88.14 Cu .. 11.86 <hr/> 100.00	0.725	1208.33	1121.36
$\text{Sn}_3\text{Cu}$ Sn .. 84.79 Cu .. 15.21 <hr/> 100.00	0.590	983.33	1200.36
$\text{Sn}_2\text{Cu}$ Sn .. 78.79 Cu .. 21.21 <hr/> 100.00	0.240	400.00	1341.869
$\text{SnCu}$ Sn .. 65.02 Cu .. 34.98 <hr/> 100.00	0.110	183.334	1666.6
$\text{SnCu}_2$ Sn .. 51.83 Cu .. 48.17 <hr/> 100.00	0.125	208.334	1977.676
$\text{SnCu}_3$ Sn .. 38.21 Cu .. 61.79 <hr/> 100.00	0.560	933.334	2298.88
$\text{SnCu}_4$ Sn .. 31.73 Cu .. 68.27 <hr/> 100.00	0.910	1516.66	2453.384
$\text{SnCu}_5$ Sn .. 27.10 Cu .. 72.90 <hr/> 100.00	0.485	808.334	2577.725

The first result which attracts attention is that none of the alloys are acted on to the same extent as pure copper; therefore the presence of tin in the alloys counteracts to a certain extent the action of nitric acid on bronzes; but the preventive influence of tin presents this particularity, that the action of the acid increases as the proportion of tin increases; thus the alloy  $\text{CuSn}_5$  is attacked ten times more than the alloy  $\text{CuSn}$ .

It should also be noticed that the quantity of metals dissolved is less in all the alloys containing an excess of copper, as well as in the two alloys  $\text{Sn}_2\text{Cu}$  and  $\text{Sn}_3\text{Cu}$ , than theory indicates, but it is especially with the alloys  $\text{Sn}_2\text{Cu}$  and  $\text{SnCu}$  that this result is observed.

TABLE 11.

*Action of Hydrochloric Acid, sp. gr. 1.10, on Alloys of Copper and Tin (Bronzes).*

Surface acted upon .....	1 cent. cube.
Quantity of acid.....	50 "
Time of action .....	1 hour.

Metals and composition of alloys.	Loss on 1 c.c.	Calculated on 1 sq. metre.	Calculated loss according to the composition of the alloys.
Copper .....	0.002	3.334	3.334
Tin .....	0.011	18.334	18.334
$\text{Sn}_5\text{Cu}$ .....	0.017	28.334	16.874
$\text{Sn}_4\text{Cu}$ .....	0.016	26.667	16.554
$\text{Sn}_3\text{Cu}$ .....	0.015	25.000	16.052
$\text{Sn}_2\text{Cu}$ .....	0.012	20.000	15.152
$\text{SnCu}$ .....	0.006	10.000	13.086
$\text{SnCu}_2$ .....	0.006	10.000	11.107
$\text{SnCu}_3$ .....	0.005	8.334	9.065
$\text{SnCu}_4$ .....	0.004	6.667	8.093
$\text{SnCu}_5$ .....	0.003	5.000	7.398

In this series of experiments, the action of hydrochloric acid upon tin is marred by the presence of copper, the action of acid on the bronzes decreasing as the quantity of copper in the alloy increases.

TABLE 12.

*Action of Sulphuric Acid (SO<sup>3</sup>HO) upon Bronze.*

Surface acted on ..... 1 cent. cube  
 Quantity of acid ..... 50 „  
 Time of action ..... 2 hours  
 Temperature..... 150° C.

  sq. metre.  
 Action upon 1 c. c. Cu = 1·678 = 2797·2  
 „  „ Sn = 3·010 = 50·17·6

Composition of alloys.	Loss on 1 cent. cube.	Calculated on 1 square metre.	Calculated loss according to the composition of the alloy.	Remarks.
<p>CuSn<sub>5</sub> 9·73 Cu 90·27 Sn <hr/><u>100·00</u></p>	·656	1093·3	4801·55	SO <sub>2</sub> given off. No HS.
<p>CuSn<sub>4</sub> 11·86 Cu 88·14 Sn <hr/><u>100·00</u></p>	·546	910·0	4754·26	Ditto Ditto
<p>CuSn<sub>3</sub> 15·55 Cu 84·45 Sn <hr/><u>100·00</u></p>	·634	1056·6	4672·32	Ditto Ditto
<p>CuSn<sub>2</sub> 21·21 Cu 78·79 Sn <hr/><u>100·00</u></p>	·525	875·0	4546·65	Ditto Ditto
<p>CuSn 34·98 Cu 65·02 Sn <hr/><u>100·00</u></p>	·632	1053·3	4240·9	Ditto Ditto
<p>Cu<sub>9</sub>Sn 51·83 Cu 48·17 Sn <hr/><u>100·00</u></p>	·797	1328·3	3866·76	Ditto Ditto

TABLE 12—Continued.

Composition of alloys.	Loss on 1 cent. cube.	Calculated loss on 1 square metre.	Calculated loss according to the composition of the alloy.	Remarks.
$\text{Cu}_3\text{Sn}$ 61.79 Cu 38.21 Sn <hr/> 100.00	.820	1366.6	3645.6	SO <sub>2</sub> given off. No HS.
$\text{Cu}_4\text{Sn}$ 68.27 Cu 31.73 Sn <hr/> 100.00	.450	750.0	3501.33	Ditto Ditto
$\text{Cu}_5\text{Sn}$ 72.9 Cu 27.1 Sn <hr/> 100.00	.372	620.0	3391.93	Ditto Ditto

In examining the results contained in this table, it will be observed that copper retards the action of the acid upon tin, none of the alloys being attacked in the ratio of the quantity of tin it contains compared with that of copper; in fact, an alloy Sn<sub>5</sub>Cu, although it contains 90 % tin and only 10 % copper, is not attacked more than an alloy SnCu, which contains 65 % tin, and 35 % copper. Again two of the alloys which contain a great excess of copper, viz., SnCu<sub>4</sub> and SnCu<sub>5</sub>, are less attacked than any of the other alloys comprised in the series, and it is difficult to understand why the two alloys SnCu<sub>2</sub> and SnCu<sub>3</sub> should be attacked with such violence as compared with the two bronzes which contain a larger amount of copper; the only explanation we shall offer of this exceptional result is, that in our experiments on the "conductibility for heat by metals and alloys," we found that those two alloys had conducting power which differed from all the rest of the alloys of copper and tin, and we submitted at that time the opinion, that it was highly probable that those two alloys were not simply mixtures of metals, but definite compounds, and the exceptional action which SO<sub>3</sub>HO has on these alloys, as compared with that it exerts upon the rest of the series, appears to substantiate this view.