The Thermo-Chemistry of the Alloys of Copper and Zinc

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XII. *The Thermo-chemistry of the Alloys of Copper and Zinc.*

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Introduction.

IT has long been known that the alloying of certain metals with each other is accompanied by evolution or absorption of heat, but in very few instances have any measurements of the thermal changes been recorded.

There is now no reason to doubt the existence of definite atomic combinations between metals, and it has therefore become a matter of considerable interest and importance to ascertain the heat of formation of these inter-metallic compounds.

LAURIE,* CHARPY,† and others have adduced evidence pointing to the occurrence of chemical combination between copper and zinc in the making of brass, and an investigation of the thermo-chemistry of their alloys appeared particularly desirable, because a peculiar interest attaches to them in connection with Lord KELVIN'S calculation of molecular dimensions.

During the progress of this work papers, dealing wholly or in part with the same subject, were published by Dr. GALT‡ and by M. HERSCHKOWITSCH §; further reference to these will be made in another place.

Choice of Method.

In making brass by the usual method, solid zinc is pushed beneath the surface of molten copper.

A violent action is frequently observed, and this is often cited as indicating the occurrence of chemical action between the metals.

Now copper melts at about 1080° C., but its temperature is doubtless higher when the zinc is added in the ordinary process of brass making, and since zinc boils at

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* 'Trans. Chem. Soc.,' 1888, p. 104.

† 'Bull. Soc. d'Encouragement,' Feb. 1896, pp. 33–34.

‡ 'Rep. Brit. Assoc.,' 1898 and 1899.

§ 'Zeits. f. Physik. Chemie,' Nov. 1898.

940° C., the violent action, before mentioned, is not necessarily the consequence of chemical union, but may be due to volatilisation of the zinc.

The difficulty of making a quantitative determination of heat evolution under such conditions appeared too great to be overcome.

The only recorded instance of such an attempt is to be found in Lord KELVIN'S lecture at the Royal Institution in May, 1897, on "Contact Electricity in Metals," where it is stated that Sir W. C. ROBERTS-AUSTEN observed an evolution of 36 calories per gramme of brass formed by the mixture of 30 parts of zinc with 70 parts of molten copper.

No details of the experiment are given.

A more promising method consists in the determination of the differences between the heats of dissolution, in a suitable solvent, of various alloys of copper and zinc and of the free metals when merely mixed in the same proportions.

This method has been adopted in the present paper.

Preparation of Alloys.

The *copper* employed in making the alloys was the best electrolytic, which had been melted, and then rolled into sheet.

Analysis showed it to be free from arsenic and bismuth, but it contained about ·15 per cent. of lead and a trace of iron.

The *zinc* used had been re-distilled. It was free from arsenic and cadmium, but contained ·06 per cent. of iron and a trace of lead.

It dissolved in hot dilute sulphuric acid only after very prolonged immersion.

Alloys containing more than 30 per cent. of copper were made by adding the requisite weight of zinc to the copper, which had been previously melted in a carbon crucible under a layer of powdered charcoal, and thorough admixture was secured by vigorous stirring with a charred stick.

In making alloys containing less than 30 per cent. of copper it was found advantageous to melt the zinc and add the solid copper to it. The latter soon dissolved if the crucible was kept at a suitable temperature.

It was easier to make an alloy, rich in zinc, of a pre-determined composition in this manner than by adding zinc to molten copper.

The alloys were cast in an iron mould yielding plates about 7 centims. × 2·5 centims. × ·5 centim. and weighing some 70 grammes.

Their outer surfaces were then removed by filing and the central portions of the ingots were used in the experiments.

The composition of each alloy was carefully determined by estimating the copper electrolytically.

In certain experiments, afterwards abandoned, Dutch metal leaf and bronze powders were used.

In order to remove the oil, which the latter always contain, they were washed in carbon bisulphide, ether, and absolute alcohol, and were then dried at 90° C.

It was hoped that a considerable range of alloys would be covered by these materials, as their colours varied greatly from reddish-yellow to pale yellow; but analysis showed that none contained less than 67 or more than 87 per cent. of copper, and it was finally concluded that they were mixtures of various alloys.

Throughout this investigation it was found absolutely necessary to use the metals in a state of very fine division in order that the time occupied by their dissolution might be kept within reasonable limits.

Those alloys which contained between 20 and 40 per cent. of copper were easily shattered by a few heavy blows in a steel mortar, and the rough powder obtained was then ground in an agate mortar.

The remaining alloys were not sufficiently brittle to be thus treated, and the tedious process of reducing them to powder with a very fine file was employed.

These filings were then sifted through the finest linen, and only the small fraction which passed was used.

This powder was then thoroughly stirred with a magnet to remove any fragments of iron which might have come from the file.

In almost every case the latter precaution was found to be unnecessary.

It has been objected that the fragments of a crushed alloy, having been strained, possess more energy than before crushing, and that this may affect the heat of dissolution. ('Report on the Chemical Compounds contained in Alloys,' Brit. Assoc., 1900.)

In various experiments the author has employed a particular alloy, sometimes in the form of rolled sheet and sometimes as filings, or, if sufficiently brittle, then either as a finely crushed powder or as filings, and in no instance has any difference of the nature suggested above become evident.

Choice of Solvent.

Those solvents which most readily suggest themselves are chlorine-water, bromine-water, and nitric acid.

The first and second are not only disagreeable to work with but are also ineffective, unless the metal to be dissolved is in a state of extremely fine division. This necessarily limits their application to the small group of very brittle alloys. A number of experiments were performed with chlorine-water as solvent.

Turning now to nitric acid, Dr. GLADSTONE* has quite recently shown that the chemical action of a mere mixture of copper and zinc upon it is different from that of the alloy containing the metals in the same proportion.

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* 'Phil. Mag.,' vol. 50, p. 231.

Since this, in itself, must introduce a difference in the heat of dissolution according as the metals are mixed or alloyed, the use of nitric acid is unsuited to the purpose in view.

Dr. GALT'S* experiments, mentioned on the first page, were made with this solvent, and the conclusions drawn from them are, therefore, open to grave doubt.

After very numerous experiments, two solvents were found which gave very satisfactory results and were not open to the objections urged against nitric acid. They are, respectively, mixtures of solutions of ferric chloride and ammonium chloride, and of cupric chloride and ammonium chloride.

Both attack the metals and their alloys rapidly, and no gas is evolved. The reactions involved are simple and give rise to a moderate evolution of heat only.

The latter point is one of considerable importance, because the rather small differences between the heats of dissolution of the metals when merely mixed and when alloyed thereby assume greater relative values, and are consequently less affected by experimental errors.

This matter is further referred to on p. 544.

Apparatus.

The *calorimeter* consisted of a thin glass beaker of rather more than 500 cub. centims. capacity.

This was supported within a highly-polished nickeled vessel by a stout rubber ring of square section, which encircled the beaker just below its rim and rested on a gallery soldered inside the metal vessel.

The latter was screened from external fluctuations of temperature by a surrounding copper water-jacket furnished with a stirrer, the air-space between the nickeled vessel and the water-jacket being covered in with a copper lid.

The beaker itself was covered with a thin ebonite sheet pierced with holes for the stirrer and thermometer.

The *stirrer* consisted of a thin sheet of mica perforated with several holes and carried by a thin glass tube, which could be actuated from a distance by a cord passing over a pulley.

The *thermometer*, by GEISSLER, of Bonn, was divided into ·01° C., and it was easy to read to ·001° C.

The position of the mercury thread was so adjusted that at the beginning of an experiment it always stood as nearly as possible at the same division, and since the rise in temperature during an experiment was usually about 1° C., the same portion of the scale was always used.

This 1° interval was found sensibly correct when compared with a standardised thermometer.

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* 'Rep. Brit. Assoc.,' 1898 and 1899.

The *water equivalent* of the calorimeter, stirrer, and thermometer was determined by the method of mixture, an apparatus similar to that used by THOMSEN in measuring heat of neutralisation being employed.

Warm water was placed in an upper protected vessel, and when its temperature had been found, a plug was removed from the bottom, thus permitting the water to flow directly into cold water of known temperature contained in the calorimeter.

In three successive experiments the following values were obtained for the water equivalent :—

15·92 grammes, 15·6 grammes, 16·3 grammes.

The mean value of 16 grammes was adopted.

In most experiments a rise in temperature of about 1° C. was arranged, as this was a sufficiently large interval to be read accurately, and yet was not large enough to necessitate the introduction of a considerable correction for radiation during the one or two minutes occupied by the process of dissolution.

All the determinations were made with the room, as nearly as possible, at 18° C., and the temperature of the calorimeter and its water-jacket was always carefully adjusted to that of the room before beginning an experiment.

SERIES I.—CHLORINE-WATER AS SOLVENT.

Although the use of this solvent was ultimately abandoned, the actual procedure in performing an experiment was exactly similar to that employed in Series II. and III., and it will therefore be described in this place.

An aqueous solution of chlorine containing 5·3 grammes per litre was prepared ; its heat capacity was found to be sensibly equal to that of the water it contained. It was first sought to ascertain the heat of dissolution of copper.

The *copper* employed was prepared—

(*a*.) By dissolution of pure copper in nitric acid, ignition of the nitrate, and reduction of the resulting oxide by hydrogen.

(*b*.) By precipitation of copper from pure copper sulphate solution by means of redistilled zinc.

The copper powder was heated in dilute sulphuric acid, washed repeatedly with water, and then with absolute alcohol.

After drying, it was heated to redness in a current of hydrogen to reduce the small quantity of copper oxide which had formed during the washing and drying processes.

Copper, thus reduced in hydrogen, retains ·6 volume of that gas, but the heat developed by the union with chlorine of the quantity of hydrogen contained in the small weight of copper used is negligible.

No difference in the thermal behaviour of the specimens of copper obtained by the different processes was observed.

The powdered copper was sifted through the finest linen obtainable, and was used at once.

It was found necessary to moisten the powder before immersing it in the liquid in the calorimeter, because entangled air prevented actual contact between them, thus preventing or seriously delaying dissolution of the metal.

For this purpose the copper was weighed on a paraffined tissue-paper tray, measuring about 3 centims. square, and a few drops of water were then thoroughly incorporated with it by means of a stirrer made of the same paper.

Since not more than ·3 gramme of water was used, its introduction produced no appreciable change in the heat capacity of the calorimeter.

[The foregoing method of preparing the copper for dissolution was applied to the zinc and all the alloys employed in this work, and was absolutely essential to success.]

Blank experiments were made to ascertain the temperature corrections to be applied for radiation, and for cooling consequent on the escape of chlorine from the free surface of the solution.

Notwithstanding every care and precaution, it was only found possible to deal with the limited number of alloys which could be easily powdered by blows in a mortar, and many of these were so difficult to dissolve that the corrections for radiation and cooling by loss of chlorine became too significant and masked any relations existing between the differences of observed and calculated heats of dissolution.

It was, however, discovered that the observed heat of dissolution of an alloy was always less than that of a mere mixture of the same composition as calculated from the ascertained heats of dissolution of copper and zinc, and that these differences were too great to be attributed to error of experiment.

This evidence of the existence of heat of combination in copper-zinc alloys induced the author to seek a more suitable solvent.

[Note on the *Heat of Solution of Chlorine in Water.*

It was easy to measure the heat of dissolution of copper powder in chlorine-water with considerable accuracy, as the process did not occupy more than one or one and a half minutes.

Four experiments, none of which differed more than ·25 per cent. from the mean, gave

$$\mathrm{Cu} \,.\, \mathrm{Cl_2Aq} = 58{,}315$$

$$\text{THOMSEN gives } \mathrm{Cu} \,.\, \mathrm{Cl_2} \,.\, \mathrm{Aq} = 62{,}710$$

$$\left.\begin{array}{l}\text{Therefore heat expended in withdrawing } \mathrm{Cl_2} \\ \quad \text{from aqueous solution by copper} \quad . \quad . \quad .\end{array}\right\} = 4{,}395$$

But the total heat evolved on the dissolution of chlorine gas in water will be greater than this by the thermal equivalent of the work done on it by the atmosphere, viz., 582 calories (at 18° C.).

i.e., $Cl_2 . Aq = 4977$ (at 18° C.).
THOMSEN* gives $Cl_2 . Aq = 2600$.

On communicating with Professor THOMSEN it appeared that the latter statement is incorrect, and he kindly gave the results of two unpublished experiments whose mean, 4870, is not very different from the author's determination.]

SERIES II.—MIXED AMMONIUM CHLORIDE AND FERRIC CHLORIDE SOLUTIONS AS SOLVENT.

If finely divided copper is immersed in a mixture of NH_4Cl and Fe_2Cl_6 solutions it is rapidly attacked with formation of cupric and ferrous chlorides.

Similarly, zinc dissolves with production of zinc chloride and ferrous chloride.

In neither case is there an evolution of gas, and the reaction takes place quantitatively.

This point was tested by dissolving weighed quantities of copper, zinc, mixtures, and alloys of the metals in separate portions of the solution, and then estimating the ferrous chloride produced.

The presence of ammonium chloride appears necessary, in practice, for the rapid dissolution of the metals and their alloys.

It may be that a thin film of cuprous chloride is first formed over the immersed metal, and that the conversion of this into the soluble cupric salt is hastened by the solvent action of the ammonium salt.

A very strong solution of the chlorides was found essential to success, and that finally employed contained in each litre 182 grammes Fe_2Cl_6 and 107 grammes NH_4Cl.

With this solution the disappearance of the metallic powders seldom occupied more than two minutes, and very frequently not more that one and a-half minutes.

Specific Heat of the Solution.

A mercurial thermometer was constructed with a cylindrical bulb of some 15 cub. centims. capacity. Two marks on the stem corresponded to 25° C. and 95° C., and in order to reduce its length, a small reservoir had been blown between the marks.

The quantity of heat evolved by this thermometer during the fall of the mercury from mark to mark was determined by immersing its bulb in 500 grammes of water in

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* 'Thermochemische Untersuchungen,' vol. 2, p. 400.

the calorimeter at the instant the mercury passed the upper mark, and withdrawing it at the instant it passed the lower.

It was found to evolve 457·4 calories.

A similar experiment was now performed with the substitution of 550 grammes of the solution for water, and the specific heat was calculated.

The results of three determinations were :—

(i.) ·752 (ii.) ·755 (iii.) ·755.

The mean of these values is ·754.

The water equivalent of the calorimeter and all its contents was therefore

$$(550 \times \cdot 754) + 16 = 430\cdot 7 \text{ grammes.}$$

Correction for Radiation.

Since the excess of temperature of the calorimeter above its surroundings at the end of an experiment was usually about 1° C. only, the correction necessary for radiation during the short period occupied by the dissolution of the metal was always very small.

The temperature was read every half minute from the beginning of an experiment. The maximum was usually reached after one and a-half or two minutes had elapsed, the greater part of the rise in temperature occurring during the first half minute.

The readings were then continued for several minutes, as the temperature slowly fell, and the rate of cooling per half minute was found.

It was assumed that during the first half minute of the rise in temperature there would be no sensible radiation loss, as a certain interval of time would elapse before the exterior of the calorimeter attained the temperature of its contents.

The radiation correction was therefore calculated by multiplying the rate of cooling by the number of half minutes, less one, occupied by the rise in temperature.

This correction was usually less than ·5 per cent. of the observed rise in temperature.

Heat of Dissolution of Copper in Ammonium Ferric Chloride Solution.

The copper was prepared exactly as for the experiments with chlorine water, and was introduced into the calorimeter on a paraffined-paper tray after it had been moistened with a very little water.

TABLE I.—Water Equivalent of Calorimeter and Contents = 430·7 grammes.

Weight of copper in grammes.	Rise in temperature ° C.	Calories evolved per gramme of copper.
·672	·279	178·3
1·7907	·751	179·8

Mean value = 179.

Heat of Dissolution of Zinc in Ammonium Ferric Chloride Solution.

Carefully sifted filings were employed in a manner similar to that described for copper.

TABLE II.—Water Equivalent of Calorimeter and Contents = 430·7 grammes.

Weight of zinc in grammes.	Rise in temperature ° C.	Calories evolved per gramme of zinc.
·4545	·9768	926
·512	1·1025	928

Mean value = 927.

In some early experiments* the author found that when nitric acid was used as solvent, a distinct difference existed between the heat of dissolution of a mixture of Cu and Zn, as determined by actual experiment, and the heat of dissolution *calculated* from the observed values for Cu and Zn when dissolved separately.

It is probable that this peculiarity may have been caused by the voltaic action of the metallic powders, in contact with each other and the liquid, influencing the mode of decomposition of the nitric acid. It was therefore deemed advisable to test this point with the present solvent.

Heat of Dissolution of Mixtures of Copper and Zinc in Ammonium Ferric Chloride.

The two metallic powders were weighed side by side, but not touching, on the same paraffined-paper tray, and after being moistened were placed in the calorimeter in the usual manner.

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* 'Proc. Chem. Soc.,' Sept. 1899.

The subjoined Table proves that if any voltaic action occurs in this case it does not appreciably affect the course of the reaction, for calculated and observed values differ by less than 1 per cent.

TABLE III.—Water Equivalent of Calorimeter and Contents = 430·7 grammes.

Weight of mixture of Cu and Zn in grammes.	Percentage of Cu in mixture.	Rise in temperature ° C.	Calories evolved per gramme.	Calories evolved calculated from Tables I. and II.
·5023	10·2	·989	850	851
·5419	18·2	·9925	789	791
·5836	32·05	·9365	690	687
·633	39·95	·926	632	628
·8203	49·4	1·068	561	558
1·00	62·27	1·067	459	461
1·2016	79·6	·9305	334	332

Heat of Dissolution of Alloys of Copper and Zinc in Ammonium Ferric Chloride.

The method of preparation and mode of dealing with the alloys was exactly similar to that previously described.

The quantity of water used to moisten the powdered alloys was so small that its effect on the water equivalent of the whole was negligible.

If we subtract the number of calories evolved by the dissolution of 1 gram of any alloy from the number calculated for a mere mixture of the same composition by the aid of Tables I. and II., the difference represents the heat of formation of 1 gramme of the alloy.

The seventh column in the following Table gives the numbers so obtained for twenty-one different alloys.

TABLE IV.—Water Equivalent of Calorimeter and Contents = 430·7 grammes.

Percentage of copper in alloy.	Weight of alloy in grammes.	Rise in temperature ° C.	Calories per gramme of alloy.	Mean calories per gramme of alloy.	Calories per gramme of mixture calculated from Tables I. and II.	Heat of formation of one gramme of alloy.
6·73	·4286 ·4878	·863 ·9836	868 869	868·5	876·5	8
12·0	·5801 ·5629	1·103 1·073	820 821	820·5	837·5	17
18·17	·6152 ·5894	1·086 1·043	761 763	762	791	29

TABLE IV.—*continued.*

Percentage of copper in alloy.	Weight of alloy in grammes.	Rise in temperature ° C.	Calories per gramme of alloy.	Mean calories per gramme of alloy.	Calories per gramme of mixture calculated from Tables I. and II.	Heat of formation of one gramme of alloy.
24·32	·7314 ·4842	1·201 ·797	707 709	708	745	37
28·18	·4496 ·5418	·702 ·849	673 675	674	716	42
32·05	·5964 ·6745	·879 ·987	635 631	633	687	54
35·53	·6846 ·7266	·969 1·0275	610 609	609·5	661·5	52
36·0	·5983 ·7822	·845 1·109	609 611	610	658	48
38·7	·8118 ·8053	1·1065 1·101	587 589	588	638	50
40·4	·41 ·6105	·5514 ·816	580 576	578	625	47
41·8	·5872 ·7318	·779 ·9608	572 569	570·5	614·5	44
42·7	·6746 ·6612	·882 ·858	563 560	561·5	607·5	46
43·9	·5193 ·4933	·669 ·633	555 553	554	599	45
45·29	·5615 ·7075	·7 ·89	537 542	539	588	49
47·85	·7126 ·8039	·866 ·979	524 525	524·5	569	44·5
50·91	·5037 ·6872	·5826 ·797	498 499	498·5	546·3	48
62·27	·6733 ·5558	·6646 ·543	424·4 419·5	422	461	39
66·8	·8669 ·9568	·7815 ·88	389 396	392·5	427·5	35
72·05	·7952 ·9008	·654 ·7315	354 349	351·5	387·5	36
82·18	1·4359 ·844	·954 ·564	286 288	287	312	25
88·92	1·2681 ·8568	·715 ·489	243 246	244·5	262	17·5

The numbers in the last column have been plotted as ordinates against percentages of copper as abscissæ, and will be discussed later.

Although the results arrived at appeared very satisfactory, it was considered advisable to confirm them by using another solvent, and a mixture of ammonium chloride and cupric chloride solutions was chosen.

Series III.—Mixed Ammonium Chloride and Cupric Chloride Solutions as Solvent.

Each litre of solution contained 1 gramme-molecule of cupric chloride and 2 gramme-molecules of ammonium chloride.

Copper is converted into cuprous chloride by this solution at the expense of the cupric salt, which suffers reduction to the cuprous condition.

The ammonium chloride serves, by its solvent action, to keep the surface of the metallic particles free from this cuprous chloride, which would otherwise delay dissolution.

Zinc placed in the solution precipitates finely divided copper from the cupric chloride, and this copper is rapidly re-dissolved, as explained above.

The solution was found to dissolve the alloys rapidly unless the percentage of copper was greater than 60, and, owing to this circumstance, the experiments were not continued beyond the alloy containing 62·2 per cent. of copper.

This difficulty arose from the fact that it was impossible to obtain those alloys which are rich in copper in a sufficiently comminuted state.

Specific Heat of the Solution.

This was found in a manner similar to that previously described.

In three successive experiments the following values were obtained :—

(i.) ·8102 (ii.) ·8102 (iii.) ·812.

Mean value = ·8108.

In the experiments which follow, the calorimeter always contained 520 grammes of the solution, and the water equivalent was

$$(520 \times \cdot 8108) + 16 = 437 \cdot 6 \text{ grammes.}$$

Experience showed that it was usually necessary to moisten the metallic powders with rather more water than when ferric chloride was the solvent, or the rate of dissolution was apt to be slow.

In the following Tables the weight of water used for this purpose has been added to the water equivalent given above.

Heat of Dissolution of Copper in Ammonium Cupric Chloride Solution.

The heat evolution in this reaction was so small that exceptionally large quantities of copper had to be employed. This necessitated the addition of some 3 grammes of water to the copper powder to bring it into a suitable condition for rapid dissolution.

Both circumstances tend to render the accuracy of the determination less than usual, but this is of small moment in the final results sought, as by far the greater portion of the heat of dissolution of the alloys is due to the zinc.

TABLE V.

Weight of copper.	Rise in temperature ° C.	Water equivalent of calorimeter and contents.	Calories evolved per gramme of copper.
3·2254 4·0741	·44 ·545	440 440·6	60 59

Mean value = 59·5.

Heat of Dissolution of Zinc in Ammonium Cupric Chloride Solution.

TABLE VI.

Weight of zinc.	Rise in temperature ° C.	Water equivalent of calorimeter and contents.	Calories evolved per gramme of zinc.
·5285 ·5001	·972 ·9214	438·5 438·5	806·4 807·8

Mean value = 807.

Heat of Dissolution of Mixtures of Copper and Zinc in Ammonium Cupric Chloride Solution.

A few experiments were made with mixtures of copper and zinc powders for the reason stated on p. 537.

The agreement between observed and calculated values in Table VII. is sufficiently close to render it unlikely that any notable thermal effect is produced by voltaic action between the metallic particles and the solution.

TABLE VII.

Percentage of copper in mixture.	Weight of mixture.	Rise in temperature ° C.	Water equivalent.	Calories per gramme of mixture.	Calories per gramme calculated from Tables V. and VI.
30·06 43·86 50·06	·7366 ·967 1·0022	·984 1·049 ·987	438·4 438·8 438·6	584·5 476 432	583 479 433·5

Heat of Dissolution of Alloys of Copper and Zinc in Ammonium Cupric Chloride Solution.

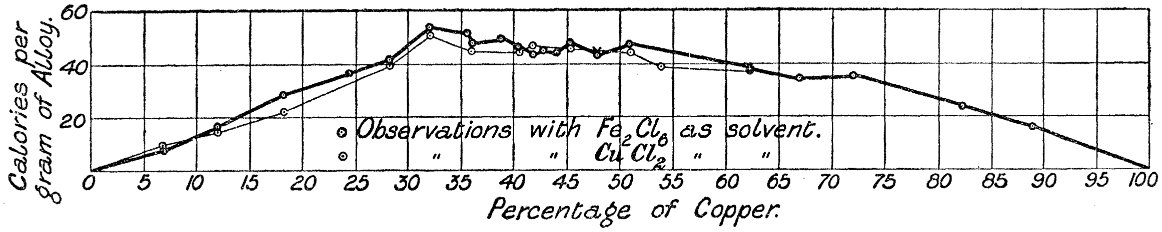
The results of these experiments are given in Table VIII., which is arranged on the plan adopted for the parallel observations with ferric chloride as solvent.

TABLE VIII.

Percentage of copper in alloy.	Weight of alloy.	Rise in temperature ° C.	Water equivalent.	Calories per gramme of alloy.	Mean value of calories per gramme.	Calories per gramme of mixture calculated from Tables V. and VI.	Heat of formation of 1 gramme of alloy.
6·73	·6201 ·591	1·06 1·007	438·3 438·3	749 747	748	757	9
12·0	·5545 ·5656	·887 ·907	438·4 438·4	701 703	702	717	15
18·17	·6377 ·6861	·942 1·018	438·7 438·3	648 650	649	671	22
28·18	·6565 ·7503	·832 ·95	438·5 438·6	556 557	556·5	596·5	40
32·05	·7755 ·7513	·912 ·89	438 438·4	515 518	516·5	567·5	51
36·0	·7843 ·8015	·884 ·901	438·2 438·2	494 492	493	538	45
40·4	·8935 ·8983	·939 ·941	438·3 438·5	461 459	460	505	45
41·8	·9383	·9595	438·5	448	448	495	47
45·29	1·0005 ·9994	·96 ·965	438·6 438·5	421 423	422	468	46
47·85	·7557 ·9838	·703 ·906	438·6 438·7	408 404	406	450	44
50·91	·9973 1·0452	·869 ·908	438·8 438·9	382 381·5	381·7	426·5	45
54·07	1·075 1·0302	·889 ·855	438·5 438·6	362·6 364	363·3	402·6	39
62·27	·9919 1·1792	·694 ·811	438·6 438·4	307 302	304·5	342	37·5

Discussion of Results.

When the results of Table VIII. are plotted in the same manner as those of Table IV., the two series of experiments strikingly confirm each other.



The small divergences from actual coincidence are not surprising, when it is remembered that each result is obtained as the difference between two large and nearly equal numbers.

It is evident at a glance that a clearly-defined maximum heat of formation is to be found in the case of the alloy containing about 32 per cent. of copper. From this point the curve drops until the alloy containing some 40 per cent. of copper is reached, whence it becomes nearly horizontal until the 50 per cent. ordinate is crossed.

Beyond this the curve drops at once, and proceeds with considerable regularity to the axis of percentages.

The significance of the foregoing lies in the coincidence of the maximum heat of formation with the percentage composition which represents an alloy of the atomic constitution $CuZn_2$.

The existence of this compound is now pretty generally accepted owing to the work of LAURIE, CHARPY, and HERSCHKOWITSCH,* and the author's results appear to confirm this conclusion.

It is also worthy of note that the upward trend of the curve, as traced from the copper end, ceases temporarily when the alloy containing about 51 per cent. of copper is reached.

This alloy corresponds very nearly with one possessing the atomic formula, CuZn. The author does not wish to lay too much stress upon this circumstance, as considerable irregularity appears to characterise the observations in the region lying between the 40 and 50 per cent. ordinates.

It was, however, the occurrence of this apparent sub-maximum, near the alloy containing 50 per cent. of copper, which led the author to test so many alloys in this region.

Taking the mean of the results afforded by Tables IV. and VIII. we may conclude that the heat of formation of 1 gramme of the compound $CuZn_2$ is about 52·5 calories.

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* See page 529.

This assumes that the alloy possessing that composition consists entirely of that compound, and this is perhaps open to question, although its physical properties and microscopic structure seem to point to its perfect homogeneity.

Since the alloy corresponding to CuZn does not show the simplicity of physical structure appertaining to the alloy $CuZn_2$, it is not justifiable to say that the heat of formation of 1 gramme of the *compound* CuZn is 46 calories, although we may make that statement with respect to the *alloy* containing copper and zinc in those proportions.

It does not appear to be known at what stage, in the making of brass, the evolution of heat of formation occurs.

Suppose that on mixing molten copper and zinc in the proportion of two parts of copper to one part of zinc (ordinary yellow brass), the heat of formation, amounting to 36 calories per gramme, is then manifested. Taking the specific heat of the molten metals as ·1 (?) we should obtain a rise in temperature of 360° C. as a result of chemical combination.

Suppose the molten copper is originally at 1200° C., that the zinc added is at 0° C., and that the latent heat of fusion of zinc is 28 (PERSON); then the temperature of the mixture, neglecting heat of formation, is given by

$$2\,(1200 - t)\cdot 1 = \cdot 1\,t + 28$$

whence

$$t = 707^\circ.$$

Adding the rise in temperature due to heat of formation, we obtain a final temperature = (707° + 360°) = 1067° C. This is well above the boiling point of zinc (940° C.), and may possibly be the explanation of the violent action often observed in making brass, although, as mentioned on p. 530, the direct volatilisation of zinc when placed in a crucible much above 1000° C. may be competent to produce the effect.

The previously mentioned work of HERSCHKOWITSCH was carried out by the dissolution of copper-zinc alloys in a water solution of potassium bromide and bromine.

His measurements were confined to two alloys containing 43·95 and 72·67 per cent. of copper, and he gives 9 calories and 12 calories respectively as their heat of formation per gramme.

As these quantities were in each case only about 1 per cent. of the heat of dissolution of the alloy, HERSCHKOWITSCH was inclined to the view that the latter possessed no heat of formation.

On reference to Tables IV. and VIII. it is apparent in many cases that the heat of formation of an alloy is about 10 per cent. of its heat of dissolution, and as the determinations are not likely to be more than 1 per cent. in error, it is quite certain that HERSCHKOWITSCH's results are inconclusive.

Molecular Dimensions of Copper and Zinc.

In Lord KELVIN's paper on "Contact Electricity of Metals" (Royal Institution, May 21, 1897), the question of the determination of the limits of the molecular dimensions of copper and zinc, by his method described in 'Nature' (p. 551, 1870), is re-opened.

On the assumption that "the work done by the attraction of two metallically connected sheets of copper and zinc when allowed to approach through any distance towards contact is the dynamical equivalent of the portion of their heat of combination due to the approach towards complete chemical combination constituted by the diminution of distance between them," Lord KELVIN showed that the molecular dimensions were less than 10^{-8} and greater than 10^{-9} centim.; for the union of plates of copper and zinc 10^{-8} centim. thick and 10^{-8} centim. apart would result in the production of 7·4 calories per gramme of brass formed.

If the distance apart were reduced to 10^{-9} centim. and the plates were each 10^{-9} centim. thick, then their union would produce 740 calories per gramme of brass formed.

Since the author finds a maximum heat of formation per gramme of brass of 52·5 calories, the limits of the molecular dimensions of copper and zinc above given would be confirmed.

The foregoing assumption that the Volta effect is capable of explanation as the result of the chemical affinity existing between copper and zinc has been subjected to much criticism (LODGE, 'Phil. Mag.,' vol. 49, 1900, p. 372).

There seems, however, to have been a tendency to under-estimate the heat of combination of these metals, for the value obtained by the author, viz., 52·5 calories per gramme of $CuZn_2$, is equivalent to 10,143 calories per gramme-molecule—a quantity quite comparable with the difference between the heats of oxidation of copper and of zinc (about 49,000 calories) on which Principal LODGE bases his calculation of the Volta effect.

Electro-deposition of Brass.

Another matter of interest lies in the bearing of these results on the electro-deposition of brass from a solution such as that of the mixed potassium-cuprous and potassium-zinc cyanides.

Here the metals unite on the cathode, and energy must be liberated.

It would probably be difficult to recognise the production of heat from this source owing to the slow rate of deposition of the alloy and to the complication introduced by the generation of heat due to the resistance of the electrolyte.

It certainly appears that a complete theory of the electro-deposition of brass must recognise the phenomenon.

Summary.

1. The production of an alloy of copper and zinc is always accompanied by evolution of heat.
2. The maximum heat of formation belongs to the alloy whose composition corresponds to the atomic formula $CuZn_2$, and amounts to 52·5 calories per gramme of alloy formed.

   This coincidence confirms the existence of a definite chemical compound, $CuZn_2$, whose heat of formation would therefore be 10,143 calories per gramme-molecule.
3. There is some indication of the possible existence of another definite compound, CuZn, having a heat of formation per gramme of alloy of about 45 calories, but the evidence is not decisive.
4. If Lord KELVIN'S calculation of the molecular dimensions of copper and zinc is accepted, the results of this paper agree with his estimate of 10^{-8} centim. and 10^{-9} centim. as limits.
5. The energy liberated in the union of copper with zinc must be taken into account in a complete theory of the electro-deposition of brass.