V. *On the Heat disengaged during Metallic Substitutions.*

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In the present communication I propose to give an account of some new investigations on the heat disengaged in chemical actions, which may be considered a continuation of my former inquiries on the same subject*. The greater number of the experiments to be detailed in this paper were made some years ago, and the conclusion at which I arrived was briefly announced in the Philosophical Magazine for August 1844. More recently, I have taken an opportunity to repeat many of my former experiments and to add new ones on the same subject, all of which confirm the general results formerly obtained.

Having originally observed that although a very limited number of bases (potash, soda, barytes and strontia) develope nearly the same quantity of heat, when a chemical equivalent of each enters into combination with an acid, yet that the greater number of bases differ most widely from one another, when so treated, while on the other hand, that different acids (taken in the state of dilute solution) produce with the same base nearly the same amount of heat, I ventured to draw the general inference that the thermal effects produced are more intimately connected with the basic, or electro-positive, than with the acid, or electro-negative element. In conformity with this view, it appeared probable that in the decomposition of solutions of neutral salts by the addition of bases or metallic bodies, the nature of the acid or electro-negative element of the compound would exercise no special influence on the result. I have already endeavoured to establish by experiment the truth of this principle in the case of basic substitutions, and, in the present memoir, I propose to extend the same general law to the other case, in which one metallic element replaces, or is substituted for another.

Few chemical actions are more simple in their final results, or admit more easily of being varied without changing the general type of the reaction, than those which form the subject of the present inquiry. When a neutral solution of any salt of the black oxide of copper, as, for example, the sulphate, the chloride, or the acetate, is precipitated by metallic zinc, the final result is the substitution of an atom of zinc for an atom of copper in the solution, and the precipitation of an atom of copper. If

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* Transactions of the Royal Irish Academy, vol. xix. pp. 228, 293. Also Philosophical Transactions for 1844, p. 21.

the physical and chemical properties of equivalent solutions of different salts of copper be compared, they will be found to present almost a complete identity, and the same remark applies to the solutions of the salts of zinc which remain after the reactions are finished. We have, therefore, every condition favourable to the production of simple thermal results. For the present object, it is not necessary to inquire in what state the metallic element exists in an aqueous solution of its salts, or what changes actually occur between the first addition of the zinc and the final precipitation of the copper; it is enough to know that the final result is the same, whether we employ a solution of an oxy-salt, or of a haloid salt.

The general result of the whole investigation may be stated in the following terms:—

When an equivalent of one and the same metal replaces another in a solution of any of its salts of the same order, the heat developed is always the same; but a change in either of the metals produces a different development of heat.

By the expression " solution of a salt of the same order" is understood, a solution in which the same precipitate is produced by the addition of an alkali, or, on one view of the composition of such salts, in which the metal exists in the same state of oxidation.

Salts of Copper with Zinc.

Two distinct series of experiments were made with the salts of the black oxide of copper and metallic zinc. In the first series, concentrated solutions were taken and introduced into a small glass vessel, in which was also placed a glass tube, open above, and containing pure zinc in a state of fine subdivision. The glass vessel, carefully closed, was introduced into a larger vessel of copper furnished with a lid. The latter was filled with water adjusted to the proper temperature and suspended in an outer vessel of tin plate, and the whole introduced into a cylinder closed with a lid and capable of being rotated*. After all parts of the apparatus had acquired the same temperature, a very sensible thermometer was introduced into the water contained in the copper vessel through a small orifice in the lid, and the position of the mercury in the tube observed. The thermometers having been removed and the orifice closed with a cork, the lid of the outer vessel was shut down, and the rotating wheel moved through half a revolution, by which means the metallic zinc was brought into contact with the copper solution. The rotation was afterwards continued for five minutes and a half, which was found to be sufficient not only to complete the precipitation of the copper, but also to diffuse the heat arising from the reaction uniformly through the apparatus. The temperature of the water was so adjusted as to render the corrections required for the heating and cooling influence of the air very inconsiderable; their amount was, however, ascertained in each experiment and the results altered accordingly.

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* For a description and representation of a similar apparatus, see Transactions of the Royal Irish Academy, vol. xix.

To remove all uncertainty as to the strength of the solutions, a considerable quantity of each salt was dissolved in water, and a portion of the solution carefully analysed by precipitating the oxide of copper. The solutions were all employed in a perfectly neutral state.

In the second series of experiments, more dilute solutions were taken, and the increment of temperature observed directly in the solution in which the precipitation occurred. The zinc, cooled to the same degree as the liquid, was introduced after the temperature of the former had been observed, and the whole rotated for a period of one minute and a half. After the final temperature was taken, a few drops of the liquid were quickly withdrawn for future examination, and the apparatus was again rotated for a period of one minute and a half. On again introducing the thermometer, the temperature of the liquid was always found to be a few hundredths of a degree higher than at the preceding observation, although the whole of the copper had been previously precipitated, and on repeating the same operation several times, nearly the same development of heat occurred on each occasion. This secondary evolution of heat arose from two distinct causes, the oxidation of the precipitated metal by the air contained in the upper part of the glass vessel, and the voltaic circle formed by the precipitated copper with the zinc in excess. The influence of the former circumstance was clearly proved by repeating the experiment with the vessel as nearly filled as possible with the solution, which considerably diminished the amount of the secondary development of heat. But without entering into a minute discussion of the efficient causes of this rise of temperature, it is sufficient for the present object to observe that the same causes must have been in operation, even in a more intense degree, during the greater part of the first period of agitation, and would render the increment then observed too high. The application of the required correction is very difficult, and the uncertainty on this point prevents absolute accuracy being attained in the following numerical results. As the most probable estimate, I assumed the correction to be equal to the increment observed during the second period of rotation, without applying any correction to this increment for the cooling influence of the air. The amount of this correction was usually about 0°·1 C. It should be carefully remembered that the precipitation was in every experiment proved to be complete at the end of the first agitation, by removing a few drops of the solution and afterwards carefully testing it. In the first series of experiments with the salts of copper, no correction was applied for this secondary development of heat, because it was impossible to ascertain its amount, which however was probably less than in the experiments of the second series.

First Series.—Sulphate of Copper and Zinc.

The solution of sulphate of copper weighed 43·3 grms. and contained 1·100 grm. oxide of copper. The specific heat of the solution of sulphate of zinc which was formed, was found by direct experiment to be 0·935, and consequently its thermal equivalent 40·5 grms. water. The apparatus in contact with the fluids contained 92 grms. copper, 20 grms. brass, and 43 grms. glass, besides the cork, &c. Its thermal equivalent, the excess of zinc included, was 17·4 grms. water. The degrees are those of the centigrade scale.

I. Air 13°·4. Increment found 2°·54, corrected 2°·53.
Water 242·6 grms. Solution and vessels (equivalent to) 57·9 grms.
II. Air 11°·8. Increment found 2°·53, corrected 2°·53.
Water 243·5 grms. Solution and vessels 57·9 grms.
III. Air 12°·0. Increment found 2°·51, corrected 2°·52.
Water 243·5 grms. Solution and vessels 57·9 grms.
IV. Air 15°·4. Increment found 2°·51, corrected 2°·50.
Water 243·6 grms. Solution and vessels 57·9 grms.

Hence we have for the heat of combination referred to 1 grm. of metallic copper as unit,

I.	II.	III.	IV.	Mean.
866°	868°	865°	858°	864°.

Chloride of Copper and Zinc.—The solution of chloride of copper weighed 43·3 grms. and contained 1·100 grm. oxide of copper. The specific heat of the solution of chloride of zinc was found to be 0·946.

I. Air 13°·5. Increment found 2°·50, corrected 2°·51.
Water 243·3 grms. Solution and vessels (equivalent to) 58·3 grms.
II. Air 14°·0. Increment found 2°·52, corrected 2°·52.
Water 238·3 grms. Solution and vessels 58·3 grms.
III. Air 14°·9. Increment found 2°·49, corrected 2°·50.
Water 244·8 grms. Solution and vessels 58·3 grms.
IV. Air 13°·6. Increment found 2°·49, corrected 2°·50.
Water 241·1 grms. Solution and vessels 58·3 grms.

We have, therefore, for the heat of combination referred to the same unit as before,

I.	II.	III.	IV.	Mean.
862°	851°	863°	852°	857°.

Acetate of Copper and Zinc.—The solution of acetate of copper weighed 43·3 grms. and contained 1·092 grm. oxide of copper. The solution of acetate of zinc formed during the reaction had a specific heat of 0·930.

I. Air 16°·7. Increment found 2°·43, corrected 2°·44.
Water 242·8 grms. Solution and vessels (equivalent to) 57·6 grms
II. Air 16°·7. Increment found 2°·43, corrected 2°·44.
Water 243·6 grms. Solution and vessels 57·6 grms.
III. Air 15°·5. Increment found 2°·40, corrected 2°·41.
Water 242·8 grms. Solution and vessels 57·6 grms.

I.	II.	III.	Mean.
841°	843°	830°	838°.

Second Series.—Sulphate of Copper and Zinc.

The solution of sulphate of copper weighed 100 grms., and contained 0·360 grm. oxide of copper. The specific heat of the solution of sulphate of zinc was ascertained by experiment to be 0·989. A large excess of zinc (4·5 grms.) in the state of fine filings was taken, in order to complete the action in the shortest possible time. The zinc had been carefully distilled, and contained not more than 0·0005 of impurity, which was chiefly lead. The glass vessel in which the experiment was performed, weighed 50 grms., and the thermal value of the entire apparatus with its contents was 106·3 grms. The whole of the copper was precipitated in the course of one minute and a half of agitation.

I. Air 17°·9. Increment found 2°·48, corrected 2°·35.
II. Air 17°·8. Increment found 2°·50, corrected 2°·37.
III. Air 17°·5. Increment found 2°·48, corrected 2°·35.

In these experiments the glass vessel was not entirely filled with the solution, and the correction for the secondary development of heat amounts, it will be observed, to 0°·13. In the two following experiments, a much smaller quantity of air was left in the vessel, and the correction was thereby reduced to 0°·05. The solution now weighed 130·0 grms., and contained 0·468 grm. oxide of copper. The thermal equivalent of the whole apparatus was 136·3 grms.

IV. Air 15°·5. Increment found 2°·40, corrected 2°·35.
V. Air 16°·0. Increment found 2°·42, corrected 2°·37.

I.	II.	III.	IV.	V.	Mean.
869°	876°	869°	857°	867°	868°.

Chloride of Copper and Zinc.—The solution contained the same weight of oxide of copper, and the zinc solution had the same specific heat as the preceding. The last experiment was adjusted in the same manner as the fourth and fifth of the foregoing series.

I. Air 17°·2. Increment found 2°·43, corrected 2°·31.
II. Air 17°·0. Increment found 2°·46, corrected 2°·34.
III. Air 17°·6. Increment found 2°·46, corrected 2°·34.
IV. Air 17°·8. Increment found 2°·44, corrected 2°·32.
V. Air 16°·1. Increment found 2°·40, corrected 2°·35.

I.	II.	III.	IV.	V.	Mean.
854°	865°	865°	858°	857°	860°.

Acetate of Copper and Zinc.—100 grms. of a solution of this salt containing 0·360 grm. oxide of copper were taken. Specific heat of zinc solution 0·987. Thermal value of the whole 106·1 grms.

I. Air 17°·3. Increment found 2°·49, corrected 2°·37.
II. Air 17°·3. Increment found 2°·50, corrected 2°·38.
III. Air 18°·0. Increment found 2°·50, corrected 2°·38.

I.	II.	III.	Mean.
875°	878°	878°	877°

Formiate of Copper and Zinc.—The solution of this salt corresponded in all respects with that of the sulphate of copper.

I. Air 17°·8. Increment found 2°·43, corrected 2°·36.

II. Air 17°·6. Increment found 2°·41, corrected 2°·34.

I.	II.	Mean.
873°	865°	869°.

Collecting the foregoing results, we find for the heat of combination from the first series,

	°
Sulphate of copper	864
Chloride of copper	857
Acetate of copper	838

And from the second series,

Sulphate of copper	868
Chloride of copper	860
Acetate of copper	877
Formiate of copper	869

The agreement among these numbers is as close as can be expected in experiments of this kind, in which other disturbing sources of heat are present, whose precise influence it is difficult to estimate. It is very plain that the heat developed is wholly independent of the acid with which the metal is combined. The results obtained in the two series, in which solutions of very different strengths were employed, differ little from one another, but an accurate comparison cannot be made, as no correction for the disturbing thermal effects was applied to the numbers of the first series. We may, however, conclude that, within the limits of these experiments, the heat developed by the same amount of metallic substitution is nearly the same in solutions of different strengths. It is probable that this observation will not be found strictly to apply to very concentrated solutions.

It is almost unnecessary to remark that if, in the course of the reaction, any chemical change occurs besides the displacement of one metal by another, the heat evolved will no longer be the same. On this account, solutions of the metallic nitrates, especially if concentrated, are not adapted for this investigation.

If we take the mean of the numbers in the second series, and adopt 3·96 as the atomic weight of copper, we shall have for the heat extricated during the displacement of

	C.		F.
1 grm. copper by zinc	868°	or	1562°
1 equiv. copper by zinc	3435°	or	6183°.

Salts of Copper with Iron.

Two distinct series of experiments similar to the preceding were made on the precipitation of the salts of copper by iron. In the first series, the apparatus and solutions were in all respects the same as in the experiments with zinc. A large quantity (from 12 to 13 grms.) of the precipitating metal was required.

First Series.—Sulphate of Copper and Iron.

I. Air 14°·7. Increment found 1°·68, corrected 1°·68.

Water 246·4 grms. Solution and vessels (equivalent to) 59·1 grms.

II. Air 14°·9. Increment found 1°·68, corrected 1°·68.

Water 244·3 grms. Solution and vessels 59·1 grms.

III. Air 14°·4. Increment found 1°·65, corrected 1°·68.

Water 243·5 grms. Solution and vessels 59·1 grms.

Hence we have for the heat of combination referred to 1 grm. copper as unit,

I.	II.	III.	Mean.
584°	580°	579°	581°.

Chloride of Copper and Iron.

I. Air 15°·5. Increment found 1°·77, corrected 1°·77.

Water 243·1 grms. Solution and vessels 59·5 grms.

II. Air 14°·2. Increment found 1°·77, corrected 1°·77.

Water 242·5 grms. Solution and vessels 59·5 grms.

I.	II.	Mean.
609°	610°	609°·5.

The greater amount of heat in the latter experiments arose from the protochloride of iron absorbing oxygen more rapidly than the protosulphate. In the next series this source of error was avoided, and the results agree better with each other.

Second Series.—In these experiments the salts were dissolved in recently boiled water, and a small bubble of air only was left in the containing vessel. Each solution weighed 126·7 grms. and contained 0·456 grm. oxide of copper.

Sulphate of Copper and Iron.

I. Air 15°·5. Increment found 1°·64, corrected 1°·62.

Heat of combination 593°.

Chloride of Copper and Iron.

I. Air 15°·5. Increment found 1°·64, corrected 1°·61.

Heat of combination 590°.

Taking the mean of the last experiments, we obtain for the heat extricated during the precipitation of

	C.		F.
1 grm. copper by iron	592°	or	1066°
1 equiv. copper by iron	2342°	or	4216°.

Salts of Copper with Lead.

Acetate of Copper and Lead.—As before, 100 grms. of a solution of acetate of copper containing 0·360 grm. oxide were taken. A large excess of lead (15 grms.) was required for complete precipitation. The thermal value of the entire was 106·0 grms.

I. Air 21°·5. Increment found 0°·89, corrected 0°·77.
II. Air 21°·5. Increment found 0°·89, corrected 0°·77.

I.	II.	Mean.
284°	284°	284°.

Formiate of Copper and Lead.—The solution was adjusted as before.

I. Air 17°·2. Increment found 0°·82, corrected 0°·72.
II. Air 17°·1. Increment found 0°·83, corrected 0°·71.
III. Air 16°·0. Increment found 0°·80, corrected 0°·70.

I.	II.	III.	Mean.
265°	269°	259°	268°.

Hence we have for the heat evolved during the precipitation of

	C.		F.
1 grm. copper by lead	268°	or	482°
1 equiv. copper by lead	1061°	or	1909°.

Salts of Silver with Zinc.

The salts of silver are easily reduced by agitating their solutions with finely divided zinc. The sulphate and acetate were selected for experiment, and the results will be found to afford a further illustration of the general principle laid down in the commencement of this paper. The secondary development of heat was also clearly manifested, and continued for a considerable period of time, but gradually diminished in intensity. The two following observations will exhibit the amount of this heat, which, in the case of the salts of silver, must be chiefly ascribed to voltaic action. The annexed numbers give the increments of heat observed at intervals of two minutes, during each of which the agitation was continued in precisely the same manner. A few drops of the liquid having been removed after the first period of agitation, gave afterwards not the slightest opalescence with chloride of sodium, showing that the metallic precipitation was then finished.

	Sulphate of silver.	Acetate of silver.
First increment . . .	1°·96	1°·94
Second increment. . .	0·14	0·12
Third increment . . .	0·12	0·12
Fourth increment. . .	0·10	0·08
Fifth increment . . .	0·09	0·06
Sixth increment . . .	0·04	0·06

The final temperature of the liquid was about 0°·7 above that of the surrounding air. The existence of a considerable amount of voltaic action was clearly shown by the evolution of hydrogen gas from the surface of the precipitated silver.

Sulphate of Silver and Zinc.—The weight of the solution taken was 100 grms. An equal portion of the same solution yielded, on analysis, 0·600 grm. chloride of silver, corresponding to 0·452 grm. metallic silver. The thermal equivalent of the solution of sulphate of zinc obtained after precipitation was 99·6 grms. water, and of the vessels, &c. 6·8 grms.

I. Air 16°·6. Increment found 1°·96, corrected 1°·82.
II. Air 15°·2. Increment found 1°·93, corrected 1°·80.
III. Air 15°·2. Increment found 1°·92, corrected 1°·79.

I.	II.	III.	Mean.
428°	424°	421°	424°.

In another set of experiments a weaker solution was employed, which gave, on analysis, 0·571 grm. chloride of silver. The thermal value of the whole was now 106·7 grms.

I. Air 18°·2. Increment found 1°·80, corrected 1°·72.
II. Air 18°·0. Increment found 1°·80, corrected 1°·72.
III. Air 18°·1. Increment found 1°·81, corrected 1°·73.

I.	II.	III.	Mean.
427°	427°	429°	428°.

Acetate of Silver and Zinc.—100 grms. of the solution gave 0·600 grm. chloride of silver.

I. Air 16°·4. Increment found 1°·94, corrected 1°·82.
II. Air 15°·2. Increment found 1°·93, corrected 1°·81.
III. Air 15°·0. Increment found 1°·93, corrected 1°·80.

I.	II.	III.	Mean.
428°	426°	424°	426°.

This result is identical with the mean number deduced from the experiments with the sulphate. We have, therefore, for the heat evolved during the precipitation of

	C.		F.
1 grm. silver by zinc	426°	or	767°
1 equiv. silver by zinc	5747°	or	10345°.

It has been already remarked that the nitrates do not in general yield the same thermal results as other salts, in consequence of the tendency of the nitric acid to decompose, which introduces other chemical actions in addition to the metallic precipitation. Approximate results were, however, obtained with the nitrate of silver. 100 grms. of a solution of nitrate of silver, containing 0·711 grm. of the dry salt, gave in three trials 2°·12, 2°·13 and 2°·11, as increments, without any correction being applied. On continuing the agitation for periods of two minutes, and observing the temperature at the end of each period, the increments followed a singular law, being at first very small, and afterwards suddenly increasing. The march of the thermometer will be readily understood by inspecting the following numbers, which give the temperatures observed at the end of every two minutes of agitation.

First increment . . .	2°·12	2°·13	2°·11
Second increment . .	0·03	0·06	0·07
Third increment. . .	0·03	0·02	0·03
Fourth increment . .	0·14	0·11	0·17
Fifth increment . . .	0·23	0·17	0·25
Sixth increment. . .	0·18	0·16	0·20
Seventh increment. .	0·13	0·15	0·23
Eighth increment . .	0·11	0·11	0·16

The sudden increase in the amount of the increment which took place after the agitation had continued for six minutes is very remarkable, and it occurred uniformly in all the experiments. It plainly shows that some new voltaic or chemical action occurred at that time, with the nature of which I am not precisely acquainted. No analogous irregularity occurred with any of the other salts of silver which were examined.

Salts of Silver with Copper.

All the solutions of silver in these experiments contained the same quantity of silver. 100 grms. of each, precipitated by hydrochloric acid, gave 0·600 grm. chloride of silver. The copper had been reduced from the oxide by hydrogen, and about 2 grms. were taken in each experiment.

Sulphate of Silver and Copper.

I. Air 13°·9. Increment found 0°·73, corrected 0°·68.
II. Air 13°·7. Increment found 0°·71, corrected 0°·69.
III. Air 12°·7. Increment found 0°·76, corrected 0°·71.

I.	II.	III.	Mean.
159°	161°	166°	162°.

Acetate of Silver and Copper.

I. Air 13°·4. Increment found 0°·68, corrected 0°·67.
II. Air 12°·8. Increment found 0°·71, corrected 0°·66.
III. Air 12°·8. Increment found 0°·71, corrected 0°·66.

I.	II.	III.	Mean.
157°	155°	155°	156°.

Nitrate of Silver and Copper.

I. Air 13°·8. Increment found 0°·74, corrected 0°·70.
II. Air 13°·0. Increment found 0°·75, corrected 0°·70.
III. Air 12°·8. Increment found 0°·77, corrected 0°·72.

I.	II.	III.	Mean.
164°	169°	169°	166°.

In this case the numbers obtained with the nitrate agree with the others. Hence we have for the heat developed during the precipitation of

	C.		F.
1 grm. silver by copper	161°	or	290°
1 equiv. silver by copper . . .	2176°	or	3917°.

Salts of Lead with Zinc.

Acetate of Lead and Zinc.—The precipitation of lead from its solutions by metallic zinc is difficult to complete in a short space of time. A large excess of zinc (8 grms.) was required and four minutes of agitation. The results on this account are only approximations. The solution weighed 130 grms. and contained 1·305 grm. oxide of lead. The thermal equivalent of the whole was 136·0 grms. water.

I. Air 17°·8. Increment found 1°·63, corrected 1°·60.
II. Air 16°·5. Increment found 1°·68, corrected 1°·65.

I.	II.	Mean.
180°	185°	182·5°.

Formiate of Lead and Zinc.—0·433 grm. of the salt employed gave 0·324 grm. oxide of lead. 100 grms. of the solution contained 1·35 grm. of the formiate.

I. Air 12°·7. Increment found 1°·74, corrected 1°·61.

I.
181°·5

Hence we have for the heat evolved during the precipitation of

	C.		F.
1 grm. lead by zinc	182°	or	327°
1 equiv. lead by zinc	2357°	or	4243°.

Salts of Mercury with Zinc.

Chloride of Mercury and Zinc.—This is the only salt of mercury which was examined. The result however is sufficient to determine the thermal position of mercury among the metals. 100 grms. of a solution containing 1·240 grm. chloride of mercury were taken. The thermal value of the whole was 106·4 grms. water. In this case no further development of heat occurred after the precipitation was completed, nor was there any disengagement of hydrogen gas. The excess of zinc, in fact, became amalgamated, which effectually prevented both oxidation and voltaic action.

I. Air 16°·6. Increment found 2°·86, corrected 2°·86.
II. Air 16°·5. Increment found 2°·85, corrected 2°·88.
III. Air 16°·4. Increment found 2°·88, corrected 2°·88.

I.	II.	III.	Mean.
332°	334°	334°	333°.

We have, therefore, for the heat disengaged during the displacement of

	C.		F.
1 grm. mercury by zinc	333°	or	600°
1 equiv. mercury by zinc . . .	4166°	or	7499°.

Salts of Platinum with Zinc.

Soda-Chloride of Platinum and Zinc.—Of the salts of platinum, the double chloride of sodium and platinum is best adapted for this investigation. The complete precipitation of platinum by zinc is more difficult, and requires a longer time than that of any of the metals hitherto examined. This renders the corrections larger and the final results less exact. To ascertain the composition of the salt employed, 0·692 grm. carefully dried were precipitated by muriate of ammonia and the precipitate ignited; 0·298 grm. metallic platinum were obtained. The solution employed in each experiment weighed 100 grms., and contained 0·721 grm. of the dry salt.

I. Air 15°·4. Increment found 2°·94, corrected 2°·64.
II. Air 16°·2. Increment found 2°·93, corrected 2°·62.

I.	II.	Mean.
902°	896°	899°

Hence we have for the heat disengaged during the precipitation of

	C.		F.
1 grm. platinum by zinc . . .	899°	or	1618°
1 equiv. platinum by zinc . . .	11085°	or	19953°.

It would have been very interesting to have extended this investigation to other cases of metallic substitution, so as to have been able to present in one complete view the quantities of heat developed in all such cases; but the facility with which some metals are oxidized, and the difficulty of precipitating others in a short space of time from their solutions, prevented me from further extending the foregoing results. For convenience, I have collected in the following table the numerical quantities already obtained:—

	Of precipitated metal.	
	1 grm.	1 equiv.
	°	°
Salts of copper and zinc	868	3435
Salts of copper and iron	592	2342
Salts of copper and lead	268	1061
Salts of silver and zinc	426	5747
Salts of silver and copper	161	2176
Salts of lead and zinc	182	2357
Salts of mercury and zinc	333	4166
Salts of platinum and zinc. . . .	899	11085

To prevent mistake, it may be right here to state that the numbers in the first column express the degrees centigrade through which one gramme of water would be heated by the precipitation of one gramme of the metal from a solution of any of its salts; and that those in the second column express the degrees through which the same weight of water would be raised by the precipitation of an equivalent (oxygen =1) of the same metal.

If three metals, A, B, C, be so related that A is capable of displacing B and C from their combinations, and also B capable of displacing C; then the heat developed in the substitution of A for C will be equal to that developed in the substitution of A for B, added to that developed in the substitution of B for C; and a similar rule may be applied to any number of metals similarly related. Several illustrations of this principle are afforded by the preceding table. Thus

1 equiv. lead displaced by zinc	2357°
1 equiv. copper by lead.	1061
1 equiv. copper by zinc	3418

The experimental result for the last case is 3435°, which in such inquiries may be considered to be identical with the theoretical number. Again,

1 equiv. copper by zinc	3435°
1 equiv. silver by copper	2176
1 equiv. silver by zinc	5611

The experimental result is 5747°, which differs $\frac{1}{43}$rd part from theory. This difference only corresponds to an error of about 0°·04 among the three experiments, and the agreement may therefore be considered satisfactory. By applying the same principle, we can easily deduce the amount of heat developed in other cases of metallic substitution. Thus an equivalent of mercury displaced by zinc should give 731 units of heat, of platinum displaced by copper 7650 units, by mercury 6919 units, &c.