II. *On the Thermal Changes accompanying Basic Substitutions. By* Thomas Andrews, *M.D., M.R.I.A., Professor of Chemistry in the Royal Belfast Institution. Communicated by* Michael Faraday, *D.C.L., F.R.S., &c. &c. &c.*

Received December 14,—Read December 21, 1843.

In a communication made to the Royal Irish Academy, nearly three years ago, I described a series of experiments on the heat evolved during the mutual reaction of acids and bases upon one another, from which the general conclusion was deduced, that when the influence of all extraneous circumstances is eliminated, the heat is determined by the basic and not by the acid element of the combination. Nearly at the same time an important memoir was published by M. Hess on thermo-chemistry, in which an opposite result was arrived at, deduced however from a very limited number of experiments, and merely announced by its author, as a probable generalization, the accuracy of which could only be determined by further researches. The principle, as stated by M. Hess, is this, that different bases disengage the same quantity of heat in combining with the same acid*.

In the present state of chemical knowledge we cannot attempt the resolution of this problem by direct experiments on the anhydrous acids and bases, even if we adopt the hypothesis, no longer universally admitted by chemists, that the proximate constituents of neutral salts are the ordinary acids and bases. Experiments performed with the concentrated acids are not adapted to yield simple results, since the mere circumstance of dilution with water produces the evolution of large quantities of heat in the case of some acids, and none, or a very slight variation of temperature in the case of others. It is for this reason that when an alkaline solution is neutralized by the addition of an equivalent of nitric acid, the heat disengaged is very different, according to the state of concentration of the acid; while the same circumstance produces little or no effect, when the tartaric acid is employed. If we institute a further comparison between the results, it will be found that while no simple relation exists between the temperatures obtained with different acids in a concentrated state, there is a very close approximation to an equal development of heat when the same base is neutralized by any dilute acid.

In many apparently simple reactions it is difficult to ascertain with certainty all the combinations and decompositions which occur, and our thermal results become proportionally difficult to interpret. Even to deduce the heat due to the combination of an anhydrous acid and alkali from that evolved when their solutions are

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* Poggendorff's Annalen, Bd. lii. 107, or Phil. Mag. v. xx. p. 1.

mixed together, is a question of very great difficulty, requiring the previous determination of many data, all of which are in few instances capable of being discovered by experiment. The liquids before mixture are, in fact, solutions of the acid and alkali in the state of hydrates, and as large quantities of heat were evolved during the formation of these hydrates, and generally also during their subsequent solution, an equal absorption of heat will take place when these combinations are destroyed. A further allowance is also required for the effect of the solution of the resulting compound. After making all these corrections it is doubtful whether the result finally obtained would not be a theoretical or imaginary number.

If we adopt the view, now generally admitted by chemists, that the hydrated acids are in reality compounds of the pure acids with water performing the functions of a base, the heat produced when a dilute acid is neutralized by a base will arise from the latter displacing an equivalent of basic water*, and the general result, before referred to, may be thus expressed. "When the same base displaces water from any of its acid combinations, the heat disengaged is nearly the same." If for basic water we substitute any base, the law will receive a very general form as follows:—

When one base displaces another from any of its neutral combinations, the heat evolved or abstracted is always the same, whatever the acid element may be, provided the bases are the same.

The following experiments were undertaken for the purpose of determining the accuracy of this principle. The base selected to displace others was the hydrate of potash, and it was always employed in a state of dilute solution. The strength of the solution was ascertained by neutralizing a determinate quantity with sulphuric acid of known strength. The required quantity was weighed in a thin brass vessel of a long cylindrical form, coated externally with copal varnish. The latter precaution effectually protected it from the action of all metallic solutions. The equivalent solution of the salt to be decomposed was contained in a thin glass jar, supported within a larger one, by means of a projecting rim. The whole was so adjusted that when the brass vessel with its contents was cautiously placed in the saline liquid it was sufficiently buoyant to float, and, at the same time, it extended through nearly the entire depth of the liquid. The weight of the two liquids taken together was 1000 grains, of which the saline solution formed about 700 grains. To bring the two liquids to the same temperature, a rapid rotatory motion was given to the inner vessel, by moving a light glass stirrer round in it. In the outer vessel a very delicate thermometer with a long cylindrical bulb was suspended. As soon as a perfect equilibrium of temperature was established between the two fluids, the position of the thermometer was carefully observed. The edge of the brass vessel was then grasped with pincers, and its contents quickly added to the saline solution. The mixture was now rapidly stirred and the new position of the thermometer noted. The brass vessel was not again introduced into the liquid after the mixture had taken place.

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* Transactions of the Royal Irish Academy, v. xix. 247.

The heat evolved, except in a few instances, did not exceed 3°; and it was so arranged that the final temperature of the liquid was from 0°·3 to 1° higher than that of the surrounding air, according to the total amount of heat. When a diminution of temperature occurred the adjustments were accordingly modified.

To this method of operating several objections will at once occur, but numerous trials have satisfied me that it gives very accurate results when the variations of temperature are not considerable. The important condition of bringing the two liquids precisely to the same temperature in a short space of time is completely attained. The principal source of error is the heating or cooling of the alkaline solution during the moment of being transferred into the outer vessel, and, if the difference between the initial temperature of the fluid and that of the air had been considerable, this would have been a serious objection to the process. The difference in question rarely exceeded 2°. As a few drops of the alkaline solution remained adhering to the interior of the vessel, an excess of 3 grains was taken, which I found to be an exact allowance for the loss. A similar portion of the saline solution adhered to the outer surface of the brass vessel, but as both liquid and salt were carried off together, the error from this cause did not in any instance amount to more than a fraction of a hundredth of a degree. The exposure to the air of the caustic solution during the few minutes occupied in equalizing the temperatures induced no sensible error.

The strength of the solution was such, that when a sulphate was employed, the entire fluid after mixture contained one per cent. of anhydrous sulphuric acid. Hence the required quantity of any salt was obtained by dividing its atomic weight by the atomic weight of sulphuric acid. The alkaline liquid contained from $\frac{1}{100}$th to $\frac{1}{200}$th of potash more than was sufficient to decompose the salt.

The thermal value in water of the bulb of the thermometer employed was 6 grains; that of the glass vessel and stirrer (the specific heat of the glass being 0·140) 68 grains; making the entire value of the vessels 74 grains. The brass vessel being removed altogether after the temperatures were adjusted is of course not included. The corresponding value of the vessels in terms of the liquid obtained is 76 grains. The temperatures found are therefore corrected for the vessels by multiplying them by 1·076.

Finally, a further correction is required for the specific heats of the solutions and precipitates obtained. But as the accurate determination of the specific heat of any substance requires great care and much time, I did not attempt to examine separately the specific heat of the product of every operation. I determined, however, very carefully the specific heats of the four principal solutions formed, and estimated the specific heats of the precipitated oxides (their weights taken in the anhydrous state) from the experiments of M. Regnault. The liquids examined were solutions (of the normal strength) of the sulphate, nitrate, and acetate of potash, and of the chloride of potassium, and their specific heats were found to be respectively 0·973, 0·975, 0·971 and 0·971*.

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* See Note at the end.

I have collected the experimental results into separate tables. The first column of each table contains the name of the salt which was decomposed; the second, its weight; the third, the change of temperature found by experiment; the fourth, the same corrected for the vessels or referred to 1000 parts of the resulting mixture; and the fifth, the same referred to 1000 parts of water.

Salts of Lime.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$CaO.NO_5$	20·6	$-\overset{\circ}{0}$·34	$-\overset{\circ}{0}$·37	$-\overset{\circ}{0}$·36
$CaO.NO_5$	20·6	−0·32	−0·35	−0·34
$CaO.S_2O_2.6HO$	32·7	−0·35	−0·38	−0·37
$CaO.S_2O_2.6HO$	32·7	−0·31	−0·34	−0·33
CaCl	13·9	−0·34	−0·37	−0·36
CaCl	13·9	−0·36	−0·39	−0·38
$CaO.\bar{A}.Aq$	22·2	−0·35	−0·38	−0·37
$CaO.\bar{A}.Aq$	22·2	−0·35	−0·38	−0·37

The nitrate was cautiously dried on a sand-bath; in one experiment the solution was neutral; in the other, it had a slight alkaline reaction. The chloride was dried at a low red heat, but not fused. Its solution was distinctly alkaline, as this salt undergoes slight decomposition from the gentlest ignition. Of the acetate, dried in a warm atmosphere, 22·64 grains yielded 12·70 grains carbonate of lime, from which the required quantity, as given in the table, was calculated.

The negative sign indicates that when potash displaces the base in these salts, a diminution of temperature takes place. The accordance of the results within the limits of the errors of experiment is perfect.

Salts of Magnesia.

The salts of magnesia are very imperfectly precipitated in the cold by caustic potash, and therefore the change of temperature indicated by the thermometer is only a part of that produced by the substitution of potash for magnesia. A depression of temperature occurred with these salts as with the preceding, amounting to between 0°·10 and 0°·15, in experiments made with the sulphate and chloride and an equivalent of potash. With a larger proportion of the latter, a greater depression of temperature occurred, but the substitution appeared to be still incomplete.

Salts of Barytes and Strontia.

In numerous experiments with the nitrates of barytes and strontia, and with the chlorides of barium and strontium, no change of temperature occurred. The solutions were taken so dilute that a mere cloud appeared on mixture, consisting chiefly of a trace of carbonate. It is true that we have no positive proof that decomposition occurs unless stronger solutions are employed and a precipitate formed, but the comparative insolubility of these bases renders it very probable that in all cases substitution does take place.

Salts of Soda.

Salt.	Weight.	Found.
$NaO.NO_5$	21·4	+0°·14
$NaO.NO_5$	21·4	+0·13
$NaO.SO_3.10HO$	40·3	+0·06
$NaO.SO_3.10HO$	40·3	+0·07
$Na\,Cl$	14·6	+0·04
$Na\,Cl$	14·6	+0·05
$NaO.CO_2.10HO$	35·8	+0·07
$NaO.CO_2.10HO$	35·8	+0·05

Salts of Ammonia.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$AdH_2O.SO_3.HO$	18·74	+0°·70	+0°·75	+0·73
$AdH_2O.NO_5$	19·98	+0·69	+0·74	+0·72
$AdH_2.Cl$	13·33	+0·70	+0·75	+0·73
$AdH_2O.C_2O_3.HO$	17·72	+0·70	+0·75	+0·73
$AdH_2O.C_4H_2O_5.HO$	25·24	+0·69	+0·74	+0·72

These experiments repeated with another thermometer gave the following results, all corrections being made:—sulphate, 0°·76; nitrate, 0°·77; muriate, 0°·76; oxalate, 0°·75, and tartrate, 0°·76. These numbers agree perfectly with one another, but their average is 0°·03 higher than the above. Before examining the thermal relations of these salts, it is necessary to ascertain that their solutions are quite neutral, as the slightest excess of acid would altogether derange the results.

I attempted to prepare a solution of the hydrocyanate of ammonia, by mixing together solutions containing an equivalent of hydrocyanic acid and an equivalent of ammonia. On decomposing this liquid by potash, an elevation of temperature occurred in different trials of 0°·87 and 0°·90, which approximates to the preceding results. The anomalies presented by the hydrocyanic acid in combining with the alkalies render this fact of some importance.

The so-called neutral phosphate and arseniate of ammonia are salts anomalous in composition, and on theoretical grounds ought to differ in thermal properties from the other ammoniacal salts. If a second equivalent of ammonia (in dilute solution) be added to a solution of the ordinary neutral salts of ammonia, no change of temperature occurs; but the same addition to the neutral phosphate produced an elevation of temperature of 0°·18. The latter salt, however, loses a part of its ammonia during evaporation with so much facility, preserving always its alkaline reaction, that I am not sure whether this is a property of the salt when of normal composition, or arose from its having lost a portion of its base before solution. When the same salt was decomposed by potash, the results were not uniform; in one experiment the heat amounted to 0°·98; in another, made with the same salt, after exposure for a very short time to a warm dry atmosphere, the heat was 1°·60; and in a third, performed with a solution of the latter previously saturated with ammonia, the thermometer rose 1°·00. If we assume the heat produced during the decomposition of potash to be 0°·99, and subtract from this 0°·18, we shall have for the heat produced by the substitution of potash for ammonia 0°·81, which is nearly the same result as before. The thermal properties of all the alkaline phosphates and arseniates are very complicated, and will require further investigation.

Salts of Manganese.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$MnO.SO_3$	18·9	+1°·00	+1°·08	+1°·04
$MnO.SO_3$	18·9	+1·00	+1·08	+1·04
MnCl.Aq	24·9	+1·00	+1·08	+1·04
MnCl.Aq	24·9	+1·01	+1·09	+1·05
$MnO.\bar{S}.Aq$	30·7	+1·11	+1·19	+1·15

The composition of the chloride and succinate was determined by converting them into sulphates. 17·05 grains of the chloride gave 12·94 grains of sulphate, and 11·24 grains of succinate gave 6·91 grains of the same, from which the above quantities were calculated. The succinate, it will be observed, produces a little more heat than the other salts. It is probable indeed that all these numbers are rather above the truth from the rapidity with which the precipitate absorbs oxygen. This produces a slight but distinct evolution of heat for some minutes after the precipitation takes place.

Proto-salts of Iron.

Salt.	Weight.	Found.	Ref. to fluid.	Ref. to water.
$FeO.SO_3.7HO$	34·5	+1°·52	+1°·64	+1°·58
FeCl.4HO	24·6	+1·57	+1·69	+1·63
FeCl.4HO	24·6	+1·53	+1·65	+1·59

The same observation applies to these results as to the preceding.

Salts of Zinc.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$ZnO.SO_3$	20·06	+1°·73	+1°·86	+1°·79
$ZnO.SO_3$	20·06	+1·76	+1·89	+1·82
$ZnO.NO_5.Aq.$	29·56	+1·68	+1·81	+1·74
$ZnO.NO_5.Aq.$	29·56	+1·65	+1·78	+1·71
$ZnO.NO_5.Aq.$	29·56	+1·69	+1·82	+1·76
ZnCl	16·87	+1·65	+1·78	+1·71
ZnCl	16·87	+1·68	+1·81	+1·74
ZnCl	16·87	+1·67	+1·80	+1·73
ZnBr	27·57	+1·65	+1·78	+1·71
ZnI	39·54	+1·68	+1·81	+1·74

The sulphate was rendered anhydrous by cautious ignition. The nitrate was evaporated till it became a solid mass on cooling. 20·17 grains of the hydrated salt left 6·85 grains of the oxide on ignition. The chloride was cautiously fused and weighed in a covered crucible. The bromide and iodide were dried on a hot sand-bath, but not fused. The three latter compounds are slightly decomposed by the heat required to deprive them of all moisture. Hence the increments of heat obtained with them must be a little below the truth. All the above salts of zinc were precipitated by an exact equivalent of potash, and the precipitate thus formed was found to consist of the hydrated oxide. But when the acetate of zinc is treated in the same manner, the precipitate which falls is a subsalt. The supernatant liquid still contains a portion of the salt of zinc, and the addition of more potash produces a further precipitate. For this reason, on precipitating an equivalent of this salt by an equivalent of potash, the thermometer rose only 1°·31. On attempting to effect a more complete decomposition by using a double equivalent of potash, the heat obtained was rather less; but it is doubtful whether the additional quantity of alkali effected a more perfect substitution, while the precipitate was, at the same time, to a great extent redissolved. This is an interesting example of an apparent exception to the law of equibasic heat arising from a corresponding anomaly in the chemical reaction.

Salts of Mercury.

The only salt of mercury adapted to these inquiries is the chloride. Half the usual equivalent of it (17·1 grains) and of the potash solution gave, in three experiments, 0°·90, 0°·86 and 0°·89, which, all corrections made and the final results doubled, correspond to 1°·89, 1°·81 and 1°·87. I have not been able to confirm this result by precipitating the oxide from any other salt. The bromide has too little solubility in cold water. The cyanuret is not decomposed by potash, and accordingly, no heat is produced when their solutions are mixed. That the potash has not decomposed the salt is further proved by the circumstance, that on neutralizing it with an acid, the same increment of temperature occurred as if the alkali had been in a free state. The sulphate and nitrate are both decomposed when their solutions are diluted. It has indeed been lately asserted that a solution of the neutral nitrate may be obtained by precipitating the chloride with nitrate of silver. This is a mistake, as the usual decomposition occurs in this case. In fact, the solution of the supposed neutral nitrate, instead of the acid reaction of the chloride from which it is formed, intensely reddens litmus paper. If a similar experiment be made with other metallic chlorides, capable of forming neutral nitrates, no perceptible change of reaction will be found to occur. These observations fully explain the anomalies which I formerly pointed out in the action of the dilute acids on the red oxide of mercury.

Salts of Lead.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$PbO . NO_5$	41·34	+2°·77	+2°·98	+2°·83
$PbO . NO_5$	41·34	+2·77	+2·98	+2·83
$\frac{1}{2}(PbO . NO_5)$	20·67	+1·39	+1·49	+2·90
$\frac{1}{2}(PbO . NO_5)$	20·67	+1·37	+1·47	+2·86
$\frac{1}{2}(PbO . \bar{A} . 3HO)$	23·64	+1·32	+1·42	+2·77
$\frac{1}{2}(PbO . \bar{A} . 3HO)$	23·64	+1·33	+1·43	+2·80

In the last four experiments half quantities were taken, but the results are all reduced to the common standard in the fifth column. After the precipitate had subsided, the clear solution above was found to be highly alkaline, capable of precipitating freely the salts of lead, and containing at the same time a small quantity of lead in solution. These facts are well known, and prove that the preceding numbers represent only a part of the heat due to the substitution of potash for the oxide of lead. Their accordance shows that the salts of lead, when similarly treated with caustic potash, give equal quantities of heat.

Salts of Copper.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$CuO . SO_3$	19·90	+2°·86	+3°·08	+2°·97
$CuO . SO_3$	19·90	+2·86	+3·08	+2·97
$CuO . NO_5 . Aq$	30·53	+2·86	+3·08	+2·97
$CuO . NO_5 . Aq$	30·53	+2·86	+3·08	+2·97
$CuCl$	16·72	+2·81	+3·02	+2·91
$CuCl$	16·72	+2·84	+3·05	+2·94
$CuCl$	16·72	+2·80	+3·01	+2·90
$CuO . \bar{A} . HO$	24·87	+3·08	+3·30	+3·18
$CuO . \bar{A} . HO$	24·87	+3·02	+3·25	+3·12
$CuO . \bar{A} . HO$	24·87	+3·06	+3·29	+3·16

The sulphate and chloride were weighed in the anhydrous state. The nitrate was taken in the state of moist crystals, and their composition determined by calcination, 8·73 grains yielding 2·83 grains oxide by calcination. The result with the acetate showing a small excess of heat, I endeavoured to discover whether it could be referred to some peculiarity in the precipitate, or in the composition of the salt. The precipitate obtained in the first experiment was collected and found to weigh 10·01 grains, or 1 per cent. more than the theoretical quantity, which, supposing an equal excess of caustic potash to have been present, could only have produced an error of 0°·03. Of the crystals employed in the last experiment, 9·40 grains being digested with nitric acid and afterwards calcined, yielded 3·74 grains oxide, which is exactly the theoretical result. It appears, therefore, that the acetate of copper, when decomposed by potash, produces about $\frac{1}{15}$th more heat than the other salts of copper.

Salts of Silver.

The nitrate is the only salt of silver I have examined, and the experiment was performed in order to ascertain the position of the oxide of silver as a thermal base. The full equivalent 42·48 grains decomposed by potash, gave 3°·88, or referred to the resulting liquid 4°·17, or to water 3°·95. Two similar experiments with half an equivalent gave nearly similar results, viz. 3°·90 and 3°·94, all corrections being made and the final results doubled to bring them to the ordinary standard.

Sesquisalts of Iron.

The bases hitherto examined being all of the form MO, it was of importance to determine how far the same principle would apply to bases of the form M_2O_3. The sesquisalts of iron appeared to be the best adapted for experiment, but it is difficult to procure them in a neutral state. The most certain method of effecting this object, is to pass a current of chlorine gas to saturation through solutions of the protosalts, expelling afterwards the excess of chlorine by heat. In this way a solution of sesquichloride may be easily procured from the protochloride, and a mixture of sesquisulphate and sesquichloride from the protosulphate. But as the resulting sesquicompounds require one half more potash for decomposition than the protocompounds from which they are derived, it was necessary, in order to preserve the usual quantity of potash, to take only two-thirds of an equivalent of the latter. Accordingly 16·40 crystallized protochloride of iron, converted into sesquichloride and decomposed by potash, gave, in different experiments, 3°·83, 3°·75 and 3°·74, which, all corrections made, correspond to 3°·97, 3°·89 and 3°·88. Of the crystallized protosulphate, 23·00 grains, treated in the same way, gave 4°·09, 4°·11 and 4°·12, corresponding to 4°·25, 4°·27 and 4°·28. These results, although not identical, present a sufficiently close approximation, particularly when the uncertainty of the original composition of the crystallized salts, and the difficulty of expelling without decomposition all the excess of chlorine, are considered. Another circumstance, whose influence it is difficult to appreciate, but which will tend to modify these results, is this, that the precipitate obtained always contains potash united by so strong an affinity to the hydrated sesquioxide that the action even of hot water produces only a partial separation. It is very probable that this may occur to a different extent with different salts, and hence may be one source of variation in the thermal effects.

On reviewing the foregoing results it will be observed, that while the effect of the substitution of potash for different bases produces thermal changes, varying from −0°·34 to +4°·28, the greatest uniformity prevails in those obtained with the salts of each separate base. It is true that in some instances slight differences do manifest themselves, but these differences, I apprehend, are in general not greater than occur in the chemical reactions. It is of course essential to a perfect uniformity of result, that exact equivalents of the salt and base should be employed, and that a complete substitution should take place. But these conditions can rarely be fulfilled. It is important, however, to remark, that, with one or two exceptions, the observed deviations are in the same direction which theory would indicate. The difficulty of obtaining most of the metallic salts in a perfectly neutral condition, and in a definite state of composition, is well known; and in the case of deliquescent compounds, a separate analysis of the specimen can rarely be employed with advantage. The variable nature of the precipitate arising from imperfect substitutions is a fertile source of divergences in the results, and the tendency to this is further increased by the necessity of performing all the experiments without the application of external heat. The formation of a subsalt produces less heat than the precipitation of the hydrated oxide, for the obvious reason that in the former case an imperfect substitution takes place. A remarkable example of this has been already cited in the action of potash on the acetate of zinc, where a great deviation from the usual development of heat is distinctly shown to depend upon the precipitate being a subsalt. The same cause, no doubt, frequently interferes with the accuracy of the result in other cases, where only a small portion of subsalt is formed. In other examples, part of the original base still remains in solution; and in others again, portions of the substituting base are carried down along with the precipitate. When we take into consideration all these sources of error, the numerous instances of perfect agreement with, as contrasted with the few examples of slight deviation from, the general law of the heat of substitution being equal for the same bases, appear to be sufficient fully to establish its accuracy.

It may be here observed that the accuracy of this principle will not be in any way affected whatever views may be adopted, as to the exact changes which occur when one base displaces another. Whether we consider the final result to arise from the simple substitution of one base into the position occupied by another, or from a series of distinct chemical changes, each producing a certain thermal effect, the general facts now established will not be the less rigorously true.

The separation of most of the bases in a solid form, will of course tend to produce heat, and as this will vary with different precipitates, the numbers for the insoluble bases cannot be exactly compared with one another. The amount of the latent heat due to precipitation is unknown, but it must be the same whenever the same precipitate is formed. The correction for this cause will, therefore, be a constant quantity for the salts of the same base, and if applied, could not affect the equality of the foregoing groups of numbers. It is important to observe, that, notwithstanding the heat due to the formation of the precipitates, a diminution of temperature occurs when potash is substituted for lime or magnesia.

On a first view this last fact appears to prove that potash is a less powerful thermal base than lime or magnesia, but a closer examination will show that it is at least premature to draw such a conclusion. It must be remembered that we are imperfectly acquainted with all the chemical changes which accompany the substitutions under consideration. We know that the substituting base existed in the state of a hydrate before mixture, and that after mixture the displaced base is also obtained in the same state. But we have no means of discovering with certainty in what state these bases exist in the solutions of their neutral combinations. If we assume that they exist in the state of hydrates, then the numbers given before will express exactly the heat arising from the chemical substitutions. But if we suppose that the potash separates from its combination with water, and the lime on the other hand unites with water during the course of the experiments, then these numbers will be the general result of a series of complicated changes. Other suppositions may be made, but we cannot prove the truth of any of them. One thing is certain, that whatever these unknown changes may be, they will be precisely similar when the bases employed are the same. Hence the foregoing experiments are sufficient to prove that with the same bases, the heat arising from basic substitutions is always the same, although the numbers may not express the entire change of temperature due to that cause.

Among the circumstances which may perhaps be supposed to influence these results, are the changes of temperature arising from the solution of the saline compounds in water,—a subject recently investigated by Mr. GRAHAM. But although it is true that a different salt remains in solution after substitution from that which was present before, yet it must be observed, that neither salt during the process assumes the solid state, and the changes of temperature in question are essentially dependent on that condition. For this reason, it appears to me that the thermal effects arising from solution are not in any way brought into action in the course of these experiments.

The same general principle will be found to include nearly all the thermal results I formerly described, as arising from the action of bases and dilute acids upon one another, and upon solutions of neutral salts. In cases where the same base (as before mentioned) displaced water from any of its combinations with the acids, the heat evolved was nearly (but not exactly) the same. On the contrary, where no basic substitution occurred, there was either none, or a very slight variation of temperature. As examples of the latter, I may refer to the absence of any variation of temperature when solutions of a neutral salt and hydrated acid, capable of combining to form an acid or double salt, are mixed. Mr. GRAHAM has indeed lately made the observation, that the formation of certain acid sulphates is attended with a diminution of temperature, but the change of temperature so produced is of small amount compared with that arising from basic substitutions. It is difficult to prove that combination actually takes place when solutions containing the proximate constituents of an acid or double salt are mixed. But, as far as I have investigated the subject, the thermal properties of the solutions thus formed are identical with those of solutions prepared by dissolving the crystallized acid or double salt in water. Thus, if we prepare solutions of crystallized binoxalate and quadroxalate of potash, and add to them exactly the quantity of potash required for neutralization, the usual heat due to the substitution of potash for water will be obtained.

I have formerly shown that there is a definite evolution of heat when solutions of the common alkaline phosphates and arseniates are mixed with a solution containing an additional equivalent of base, while no change of temperature occurs when a solution of the pyrophosphate of soda is similarly treated. In the former case, it has been shown by Mr. GRAHAM that an atom of basic water is displaced by an atom of alkali; in the latter case, no basic water is present.

In the preceding observations it has been assumed, that if the union of two substances be attended with the evolution of a certain definite quantity of heat, their separation will be attended with the absorption of the same quantity of heat. Although this proposition in the abstract is very probable, it requires to be demonstrated by direct experiment, and it is the more important to do so, as it will furnish, if true, a means of verifying the accuracy of our results. The reactions now described enable us to test it by experiment in one particular set of cases. In fact, if we take three bases, such as potash, oxide of copper, and water, capable of displacing one another in the above order, and if we measure the changes of temperature produced when the first and second, first and third, and second and third bases displace one another, then the change of temperature arising from the first substitution should be equal to the difference between the changes of temperature produced by the two latter. A few examples will illustrate this point.

The numbers expressing the heat developed when the nitrate of water is decomposed by potash and lime are 6°·76 and 7°·20. The difference of these numbers is −0°·44, indicating that a depression of temperature to that amount ought to take place when the former base is substituted for the latter. We have before seen that the result of the direct experiment is −0°·37. In this and the following cases, the temperatures corrected only for the vessels are adopted, because I have not determined the specific heats of the metallic solutions. The error in the comparison from this circumstance is wholly insignificant.

The heat produced in two experiments in which sulphate of water was decomposed by potash was 7°·24 and 7°·22. The same compound decomposed by ammonia gave in different trials 6°·40, 6°·53 and 6°·51. The difference of the means of these numbers is +0°·74. The direct experiment gave in one experiment +0°·75, in another +0°·78.

The corresponding number which expresses the substitution of oxide of zinc for water in the sulphate of water is 5°·40, and this taken from 7°·22 leaves 1°·82 for the heat due to the displacement of oxide of zinc by potash. The direct experiment gave 1°·87.

Two experiments were made to determine the heat arising from the substitution of oxide of copper for the base in the nitrate of water. In one of these experiments the hydrated oxide was taken; in the other, the anhydrous oxide, obtained by precipitating a hot solution of the sulphate of copper by caustic potash. The results agreed closely with one another, being 3°·52 and 3°·53. Taking the mean of these numbers from 6°·76, we have 3°·23 to express the heat due to the substitution of potash for oxide of copper. The result of the direct experiment was 3°·08.

A similar comparison cannot be made with the salts of magnesia or lead, because an imperfect substitution takes place when their solutions are precipitated by potash.

If we compare in like manner the other results contained in the paper before referred to, it will be found that the differences between theory and experiment rarely exceed 0°·3,—a close approximation when the defective method of investigation formerly employed, and the great difficulty of obtaining accurate results with the insoluble bases are considered.

It may be remarked that there is no notable difference in the heat developed during the solution of the oxides of zinc and copper in the hydrous and anhydrous states, which makes it probable that the heat due to the combination of those bases with water is not considerable.

The preceding experiments appear to me to be sufficient to establish the accuracy of the general principle already stated, that when one base displaces another from any of its neutral combinations (all being taken in the state of dilute solution) the heat is always the same with the same bases, but in general different with different bases. The small deviations from this law in the case of the ordinary bases are not greater than we observe in other investigations connected with heat; and I have before pointed out many circumstances which tend to account for some of these deviations. The results obtained during the decomposition of the salts of water present more remarkable anomalies, as I have formerly shown. Of these, the greater development of heat during the neutralization of the dilute sulphuric acid by alkaline solutions deserves particular notice, and still remains unexplained. The anomalies presented by the oxide of mercury and hydrocyanic acid, I have partly traced to their source. But the other results approximate too closely to one another to leave any doubt that the same principle applies to the decomposition of the salts of water as well as to that of the salts of other bases.

I have not succeeded in connecting the thermal developments, as given by experiment, with any other property of the bases. In the following list I have arranged the bases hitherto examined in the order of the thermal results, attaching to each the number expressing the change of temperature produced when its salts are decomposed by potash.

CaO	−0°·36	ZnO	+1°·74
BaO	0·00	HgO	+1·86
SrO	0·00	PbO	+2·82+
NaO	+0·08	CuO	+3·00
AdH_2O	+0·74	AgO	+3·93
MnO	+1·07	$Fe_{\frac{2}{3}}O$	+4·09
FeO	+1·60		

Supplementary Note on the Determination of the Specific Heats of Fluids.

The accurate determination of the specific heats of fluids is of so much importance in all inquiries connected with the heat of combination, that I have taken some pains to introduce greater simplicity and accuracy into the methods hitherto employed for that purpose. The process I am about to describe is a modification of that adopted by M. Regnault in his valuable researches on the specific heats of simple and compound bodies, and I am also indebted to the same accurate philosopher for a knowledge of the most important precautions to be taken in inquiries of this kind.

The general principle of the following method is to compare the increments of temperature produced by the cooling of a hot body in water and in the fluid under examination. But instead of taking, as is usually done, a ball of heated metal, whose temperature at the moment of immersion cannot be known with absolute precision, I employed a thermometer with a very large reservoir, and so adjusted that the mercury does not appear in the stem till it is heated to nearly the boiling point of water. The cylindrical reservoir is about two inches long, and half an inch in diameter. A mark is placed on the stem corresponding to 201° Fahr., which point is situated about an inch and a half from the reservoir. This instrument is easily heated by means of a very simple apparatus till the mercury rises a little above the mark.

The first step of the process is to determine accurately the thermal value of the reservoir with a small portion of the stem adjacent to it in terms of water. For this purpose, a certain weight of water is placed in a cylindrical vessel of thin brass, which is suspended within a larger vessel of tin plate. A very delicate thermometer, with a long cylindrical bulb (capable of being read with ease to $\frac{1}{50}$th part of a degree), is suspended in the water, and the whole is so arranged that the initial temperature of the fluid is about 5° below that of the surrounding air.

The observer, previously agitating with a very light glass stirrer the water in the brass vessel, reads the temperature to an assistant, who notes it down and also marks the time. The former then removes the large thermometer from the heating apparatus (the disturbing influence of which is carefully prevented by a wooden screen) and, holding it at a suitable distance from the water, watches the descent of the mercury till it reaches the mark, when he instantly immerses it. The time of immersion is again noted, and the whole is gently agitated for $3\frac{1}{2}$ minutes in the fluid. The temperature of the latter having now always attained a maximum, the new position of the thermometer is observed. The final temperature is never allowed to be more than 2° higher than the air.

The corrections for the heating and cooling influence of the air are very small when all the above conditions are fulfilled. They must not, however, be neglected. The rate of heating for each degree of depression per minute was found to be 0°·01, and as from 12 to 20 seconds usually elapsed between the observation of the initial temperature and the immersion of the heated instrument, the correction for that period of the observation was easily made. It was assumed that during the minute subsequent to the immersion, the heating and cooling processes counterbalanced one another; and the correction for the last 2½ minutes was made on the hypothesis that the fluid during that period was at the final maximum. The rate of cooling was found to be about 0°·012 per minute, for each degree of excess, the fluid being kept in constant agitation.

Knowing the weight of the water, the value in terms of water of the different parts of the apparatus, the temperature gained by the water and lost by the instrument, we possess all the data necessary to calculate the thermal value of the latter in terms of water.

By repeating the same experiment with an equal bulk of the liquid whose specific heat is required, we obtain the thermal value of the same instrument in terms of the liquid. From these values the specific heat may be calculated. An equal bulk of the liquid is employed in order to have the instrument immersed in all cases to precisely the same depth, and, for a similar reason, it ought to be always introduced in a perpendicular direction into the fluid and maintained in the same position during the agitation. Before calculating the final result, it is necessary to obtain an approximate one, in order to find the thermal value of the brass vessel, &c. in terms of the liquid. In actual practice this is easily effected without involving any sensible error. If the specific heat of the liquid differ considerably from that of water, the correction for the heating and cooling influence of the air must also be modified.

The weights of the different parts of the apparatus and their value in water are as follows:—

Mercury in bulb of thermometer by which the increment of temperature was measured 300 gr. × 0·033	9·9
Glass in bulb and immersed portion of stem 24 gr. × 0·14	3·3
Glass stirrer 20 gr. × 0·14	2·8
Brass vessel 420 gr. × 0·094	39·5
Value of entire apparatus	55·5

The value of the apparatus in terms of the following solutions is 57·0 grains.

If we now make

D. The difference between 201° and the final temperature of the liquid, or the heat lost by the instrument.

e. The excess of the final temperature above the air.

I. The increment of temperature observed.

I^c. The increment corrected.

F. The weight of the fluid.

Vss. The value of the apparatus in terms of the fluid.

X. The value of the instrument in terms of fluid.

Distilled Water.

	I.	II.	III.	IV.	V.
D.	132°·0	131°·7	132°·8	132°·5	132°·8
e.	1·1	0·3	0·4	1·4	2·2
I.	6·38	6·45	6·46	6·40	6·40
I^c.	6·39	6·44	6·45	6·43	6·45
F.	1234·5	1234·5	1234·5	1234·5	1234·5
Vss.	55·5	55·5	55·5	55·5	55·5
X.	62·45	62·60	62·65	62·60	62·65

Mean value in terms of water 62·59.

Solution of Sulphate of Potash (100 parts contain 2·18 salt).

	I.	II.	III.
D.	131°·8	132°·2	132°·4
e.	1·3	1·1	1·0
I.	6·38	6·42	6·45
I^c.	6·41	6·43	6·46
F.	1264·5	1264·5	1264·5
Vss.	57·0	57·0	57·0
X.	64·27	64·28	64·48

Mean value in terms of solution 64·34.
Specific heat 0·973.

Solution of Nitrate of Potash (100 parts contain 2·53 salt).

	I.	II.	III.
D.	135°·8	135°·5	135°·7
e.	1·1	1·4	1·0
I.	6·59	6·56	6·57
I^c.	6·60	6·59	6·58
F.	1264·5	1264·5	1264·5
Vss.	57·0	57·0	57·0
X.	64·23	64·27	64·08

Mean value in terms of solution 64·19.
Specific heat 0·975.

Solution of Chloride of Potassium (100 parts contain 1·86 salt).

	I.	II.	III.	IV.
D.	132°·8	132°·4	132°·3	132°·4
e.	1·6	1·6	1·6	1·6
I.	6·45	6·43	6·42	6·43
I^c.	6·48	6·46	6·45	6·46
F.	1264·5	1264·5	1264·5	1264·5
Vss.	57·0	57·0	57·0	57·0
X.	64·48	64·48	64·43	64·48

Mean value in terms of solution 64·47.
Specific heat 0·971.

Solution of Acetate of Potash (100 parts contain 2·45 salt).

	I.	II.	III.
D.	133°·5	132°·9	133°·1
e.	1·8	2·1	1·8
I.	6·46	6·44	6·46
I^c.	6·50	6·49	6·50
F.	1264·5	1264·5	1264·5
Vss.	57·0	57·0	57·0
X.	64·34	64·53	64·54

Mean value in terms of solution 64·47.
Specific heat 0·971.