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THE ADIABATIC DETERMINATION OF THE HEATS OF SOLUTION OF METALS IN ACIDS.

[FIRST PAPER.]

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Introduction.

The heats of solutions of metals in acids are among the most essential and fundamental of thermochemical data. The heats of formation of all the metallic compounds depend upon them, because through them the heat values are referred back to the element. Hence it is highly important for exactness in thermochemistry that these values be determined with great precision.

As a matter of fact, in the past certain difficulties have interfered with the perfection of the measurements. First and foremost among these is the fact that the solution of a metal requires much time, and therefore the always somewhat uncertain correction for cooling in the usual method becomes a serious fraction of the whole rise of temperature. In the second place, the method generally used, namely, the plunging of a weighed sheet of metal into acid, and then withdrawing it, checking the reaction as soon as possible, and determining the amount dissolved by loss in weight, is open to serious criticism. It is impossible that the withdrawal should be so quick as to introduce no error in the results.

The new method of adiabatic calorimetry, recently used at Harvard, seems to be especially suitable for such cases as this, and accordingly, the present investigation concerns itself with the application of this method to the solution of metals in acids. This method of calorimetry avoids wholly the cooling correction by surrounding the calorimeter with a jacket, having always precisely the same temperature as the calorimeter itself. The jacket contains an alkali, and as the reaction progresses within the calorimeter, enough acid is added, drop by drop, to this alkali to change its temperature at exactly the same rate as that of the calorimeter proper.

This method overcomes entirely the first fault which exerted an especially detrimental effect upon the early determinations of the heat of solution of metals—this fault being, namely, the large cooling correction, because of the slowness of the process. The second difficulty was overcome by another device. Instead of dissolving only a part of a large metal sheet or net, we placed the metal in a finely divided condition in a basket, and the reaction was allowed to continue until all which had been placed in the basket was completely dissolved. The calorimetric method allows plenty of time—a slow reaction is as well measured as a quick one. Hence this procedure involves no difficulty, but affords a satisfactory method of overcoming the faults in the doubtful mode of operation previously adopted.

In carrying out experiments by this method, it was found that as the effectiveness increased, another error which also must have affected previous determinations was uncovered. In reactions of this kind the solution is not always mixed very thoroughly during the progress of the reaction, and the thermometer does not always fairly represent the average temperature, unless the stirrer is very active. Hence, according to the old method, the cooling correction is not properly calculated, and according to the new method the jacket is not maintained at the right temperature. In either case inaccurate final results will be obtained. Obviously, a correct result is to be hoped for only when the stirring is so active that the temperature is nearly the same throughout the calorimeter. Our experience leads us to believe that early work of this kind did not maintain sufficient equality of temperature. That exceedingly concordant results may be obtained if these precautions are all heeded is shown by the results to be given later.

In brief, this paper presents an account of the highly successful application of the new method of adiabatic calorimetry to one of the most important series among thermochemical data.
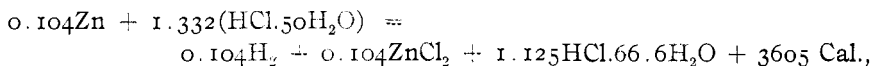
Discussion of Earlier Work.

Apparently Thomsen[1] alone, among earlier thermochemists, has measured the heats of solution of most of the metals in acids. We owe much to this eminent investigator, but it is not surprising that his pioneer work, carried out at a time when chemistry was a far less precisely quantitative science than at present, should not have attained a degree of accuracy which is now attainable. A brief description of his method is not out of place. The calorimeter which he used consisted of three concentric cylindrical cans which were insulated from one another by means of air spaces. The inner of these cans constituted the calorimeter proper and was made of platinum. The stirrer was a single ring which was moved vertically up and down by mechanical means; since it will be shown in the present work that two such rings vibrating in a similar fashion did not effect thorough mixing, it is quite evident that the stirring which he employed was entirely inadequate. The thermometer, which had been carefully standardized, was graduated to tenths and could be read by means of a telescope to 5 one-thousandths of one degree—a degree of precision much below the modern standard. A single cover on the outside cylinder shielded the apparatus from above and through it the stirrer and thermometer passed. The metal was introduced in a sheet or coil of netting, and was withdrawn, washed and dried after a suitable time. His results are therefore open to the two main objections, which were emphasized in the introduction, namely, a large cooling correction and an inaccurate method of introducing the metal. Besides these, other sources of error, which must be eliminated from accurate work, were overlooked by him. When fine bubbles of gas escape from a solution, they carry away with them small particles of the liquid, and, although the quantity of liquid so carried away is small, yet it is by no means negligible. Moreover, his metals were not very pure, being the best he could obtain commercially. The amounts of impurities were determined by analysis, and corrections were applied, entirely ignoring any possible heat effects due to alloying of the metals. The acids mainly used by Thomsen were of two concentrations—$HCl.25H_2O$ and $HCl.50H_2O$. From the results obtained with these acids he calculated the values for acid of the concentration $HCl.200H_2O$. To do this he determined the heat of dilution of the acid from the initial to the final concentration and subtracted the result from the heat of solution of the metal, assuming that the solution of the salt in excess of acid is the same (thermochemically) as its solution in the same quantity of pure water—
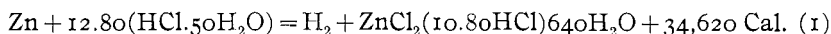
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[1] Thomsen, *Thermochemische Untersuchungen*, Vol. III, page 217. Hess and Favre and Silbermann determined the heats of solution of zinc in hydrochloric and sulphuric acids. Their results have been discussed by Thomsen (*Thermochem. U.*, Vol. III, 273).

an assumption which is plainly hazardous and will be shown later to be incorrect.

A study of one of Thomsen's actual experiments will make clear the error into which he fell as well as indicate the correct method for making this calculation. One of the experiments on zinc, in which he dissolved 6.82 grams of zinc in 1248.7 grams of acid of the concentration HCl. $50H_2O$, may be selected.[1] The actual conditions of his experiments are accordingly represented by the equation
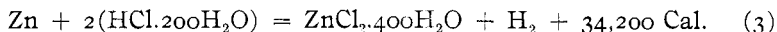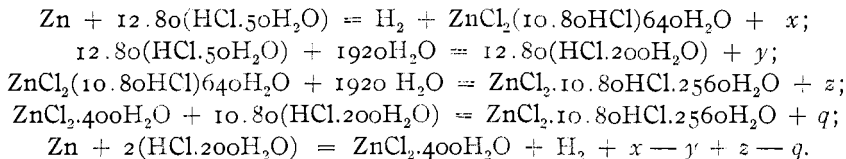
$$0.104Zn + 1.332(HCl.50H_2O) =$$
$$0.104H_2 + 0.104ZnCl_2 + 1.125HCl.66.6H_2O + 3605 \text{ Cal.},$$

or multiplying by 9.61,

$$Zn + 12.80(HCl.50H_2O) = H_2 + ZnCl_2(10.80HCl)640H_2O + 34,620 \text{ Cal. (1)}$$

He then determined the heat of dilution of the acid $HCl.50H_2O$ to HCl. $200H_2O$.

$$2(HCl.50H_2O) + 300H_2O = 2(HCl.200H_2O) + 420 \text{ Cal.[2]} \quad (2)$$
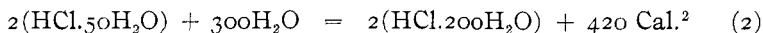
Now by subtracting equation (2) from (1) he claimed to obtain:

$$Zn + 2(HCl.200H_2O) = ZnCl_2.400H_2O + H_2 + 34,200 \text{ Cal.} \quad (3)$$

Evidently this result (equation 3) can only be obtained by a set of reactions similar to the following:

$$Zn + 12.80(HCl.50H_2O) = H_2 + ZnCl_2(10.80HCl)640H_2O + x;$$
$$12.80(HCl.50H_2O) + 1920H_2O = 12.80(HCl.200H_2O) + y;$$
$$ZnCl_2(10.80HCl)640H_2O + 1920 H_2O = ZnCl_2.10.80HCl.2560H_2O + z;$$
$$ZnCl_2.400H_2O + 10.80(HCl.200H_2O) = ZnCl_2.10.80HCl.2560H_2O + q;$$
$$Zn + 2(HCl.200H_2O) = ZnCl_2.400H_2O + H_2 + x - y + z - q.$$

That is to say, *all* the acid corresponding to a gram atom of zinc must be diluted, instead of only 2 moles. Moreover, the resulting solution of the salt in the excess of acid must be diluted an equivalent amount, and the further change of internal energy, brought about by mixing the pure dilute salt solution (in this case $ZnCl_2.400H_2O$) with the proper quantity of acid of equivalent concentration must be determined. It is amazing that no one has ever discovered these errors of logic before. In working out these equations, no account has been taken of the temperature at which the last three reactions should be performed, whether at the initial temperature or final temperature of the experiments for equation (1). This is a matter of considerable importance and will be fully discussed later.

Having thus shown the chief causes of inaccuracy in Thomsen's work—which apply with even greater force to earlier experimenters—we may turn to the present series of experiments, and review the various pre-

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[1] *Thermochemische Untersuchungen*, Vol. III, page 272. The mean value 34400+ 220 c, the heat of vaporization of the water with which the hydrogen was saturated.

[2] *Ibid.*, Vol. III, page 242.

cautions yielding better results. First the preparation of the materials will be discussed, then the calorimetric apparatus, and finally the details of manipulation and the results.

Materials.

The significance of work of this kind depends greatly on the purity of the materials employed. There is, of course, no object in determining accurately the heat of solution of a substance containing unknown impurities in appreciable amount.

The materials used in this work were most of them of a high order of purity. Where very pure substances were unattainable, the impurities were determined and due allowance for them was made.

Hydrochloric Acid.—Three concentrations of hydrochloric acid were used, namely, $HCl.8.808H_2O$, $HCl.20.0H_2O$, and $HCl.199.8H_2O$. Chemically pure acid was diluted to these concentrations and the exact values were verified by gravimetric analyses in which the chlorine was precipitated with silver nitrate.

Zinc.—Two preparations of zinc were employed in the research. The first sample consisted of fine crystals obtained by electrolysis from an ammoniacal zinc sulphate solution. A solution containing zinc sulphate had been previously oxidized with chlorine water and the iron precipitated by digestion with freshly made zinc hydroxide. This process was repeated until the precipitate no longer became colored on standing. Zinc sulphate was crystallized from the filtered solution and subsequently recrystallized three times from pure water. The pure salt was dissolved in distilled water, ammonia was distilled into it until the precipitated hydroxide had completely dissolved, and the solution electrolyzed between platinum electrodes under a high current density. In this way very finely divided crystals were obtained, which offered later a large surface to the action of the acid. The metal was removed from the solution by means of a glass instrument resembling a rake, and was preserved under a dilute solution of ammonia. It was washed with dilute ammonia until all zinc salts adhering to it were removed, and immediately afterwards was speedily washed with pure water. As quickly as possible the water was replaced by three washings with alcohol, and this treatment was followed by three more washings with ether.[1] The metal was dried by being placed in a vacuum desiccator containing sulphuric acid.

The surface of the zinc obtained in this fashion, although it appeared very bright, was covered with a very thin film of oxide. This covering was only perceptible from the fact that when thrown upon dry mercury, the metal amalgamated very slowly or not at all; indeed, it could be

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[1] The alcohol was purified by being twice distilled from quicklime. The ether was distilled after standing for several days over calcium chloride.

stirred into the mercury without amalgamating. If, however, the mercury was covered with a dilute solution of ammonia and the zinc thrown upon it, amalgamation proceeded with great rapidity. This fact was utilized to determine the amount of oxide present. A weighed quantity of zinc was amalgamated under a dilute solution of ammonium hydroxide, which was then poured off, neutralized and titrated with a standard potassium ferrocyanide solution. The solution must have contained all the oxide, as the surface of the mercury was perfectly bright. The results show that only a very small part of the metal had been oxidized.

DETERMINATION OF ZINC NOT AMALGAMATED.

	Wt. zinc.	Vol. of $K_4Fe(CN)_6$ soln. cc.	Equivalent of zinc oxide. Gram.	Wt. of zinc oxidized in 7.5 grams.
1	1.5	0.14	0.0006	0.0025
2	1.5	0.12	0.0005	0.0020

That is to say, the oxide cannot exceed 0.037 per cent. of the weight taken, hence even if the oxide were insoluble in acid, the error from this source could not exceed this amount. Probably the observed quantity is unduly exaggerated by the solution of some metallic zinc in ammonia, during the act of amalgamation, when electrolytic effects would occur. Therefore 0.03 per cent. is a safe estimate of the combined zinc present in the metal. But a part even of this was probably present as ammoniacal sulphate in solution and not as oxide. When a metal is deposited from a solution, as the zinc crystals had been, it encloses minute drops of the mother liquor, just as do also crystals of most if not all salts;[1] and the quantity of included solution is greater the faster the metal is deposited. The quantity of enclosed mother liquor was determined in the present instance by fusing the metal in a current of dry nitrogen and absorbing the water with phosphorus pentoxide. Blank experiments, in which dry air was passed through the apparatus for a long time, served to eliminate any constant errors of experimentation.

VOLATILE MATERIAL ENCLOSED BY CRYSTALLIZED ZINC.

	Weight of zinc.	Weight gained by pentoxide tube.	Blank.	Weight of volatile matter from zinc.
1	3.00	0.00105	0.0001	0.00095
2	3.00	0.0011	0.0001	0.0010
3	3.00	0.0010	0.0001	0.0009
			Mean,	0.00095

Since the solution used for electrolysis contained about 20 per cent. of zinc sulphate, the total weight of enclosed mother liquor in 3.0 grams of zinc was 0.0012 gram, or 0.04 per cent. of the original weight of metal. This small amount of enclosed mother liquor must have contained about

[1] See Richards, Z. physik. Chem., 46, 189 (1903); also Hulett and DeLury, THIS JOURNAL, 30, 1812.

0.1 milligram of zinc, which must have appeared along with the oxidizod portion in the amalgamation experiments, and should be subtracted from the quantity there discovered. Otherwise the metal was very pure; a careful qualitative analysis failed to show the presence of any other metal.

The sum total of impurity found in the zinc is thus not over 0.07 per cent., but to apply this correction in full would overstep the mark.

Both zinc oxide and hydroxide, as well as the ammoniacal mother liquor, give out heat when dissolved in acid. The two former yield about two-fifths as much heat as metallic zinc would, and the mother liquor was found to yield about one-twelfth as much. Hence, considered from a thermochemical point of view, the zinc must have acted as if it contained only about 0.055 per cent. of impurity, a correction which is applied in the following pages.

The second sample was Merck's pure zinc ("reagent") in granulated form, which had been pounded into thin sheets on an anvil. Both the hammer and the anvil were carefully cleaned before being used, and the pieces were polished by shaking with sand and alcohol afterwards. This zinc was very pure and contained, as far as careful testing could show, only a very slight trace of iron, which may have been introduced during the process of pounding. No attempt was made to determine the amount of iron present, since scarcely a weighable amount of ferric hydroxide was precipitated from seven grams of zinc. No other impurities were found, so that no correction for impurities was made with this material..

Aluminium.—The aluminium used for this work was in the form of a thin foil—the purest that could be obtained on the market. It contained negligible traces of iron and sodium and a small quantity of silicon, which was carefully estimated.

The determination of silicon in a metal of this type is by no means an easy matter. Some of the contaminating element is present in an uncombined form and some combined or alloyed with the metal; the former portion appears as silicon when the metal is dissolved, the latter partly as hydrated silica and partly as hydrogen silicide.[1] The silica is partly precipitated and partly dissolved colloidally. Hence a number of steps have to be taken in order to determine the total amount. In the first place, the aluminium was dissolved in hydrochloric acid and the precipitate collected and ignited in hydrogen. This gave the combined weight of silica and silicon precipitated. Ignition in air then oxidized the silicon to silica, giving a measure of the quantity of the former, and treatment with hydrofluoric acid showed how little of other impurities had been retained by the precipitate. The silica which remained in solution

[1] Joseph W. Richards.

in the acid was found exactly as in a silicate analysis, according to the method recommended by Hillebrand.[1] The silicon which escaped as hydrogen silicide was determined by passing the impure hydrogen from a known weight of the metal through a solution of caustic alkali made from the metal and water in platinum, determining the silica in this solution. Parallel analyses were made with material from several sheets of similar material, the samples showing considerable uniformity. The following tables give the analytical results:

SILICON IN THE PRECIPITATE.

	Weight of aluminium.	Weight of residue after ignition in hydrogen.	Weight of residue ignited in air (silica). Milligrams.	Per cent. of silicon.
1	0.75	....	5.7	0.35
2	0.75	....	5.4	0.33
3	0.75	....	5.1	0.32
4	0.75	0.0030	...	....
5	0.75	0.0030	...	....
		0.0030	5.4	0.34

SILICON IN THE SOLUTION.

Weight of aluminium.	Weight of silica found.	Per cent. silicon.
0.7500	0.0008	0.050
0.7500	0.0006	0.038
	Average,	0.044

SILICON IN THE GAS.

Weight of aluminium.	Weight of silica found.	Per cent. silicon.
1.80	0.0008	0.021
1.75	0.0006	0.016
	Average,	0.018

Thus the total weight of the element silicon was found to be 0.40 per cent. of the original weight of the metal taken.

Assuming that the difference between the results of Analyses 1, 2, 3 and 4, 5 gives the weight of oxygen needed to convert uncombined silicon into silica, the silicon present as such in the residue must have been 0.0021 gram.

In computing the effect of the impurity on the heat of reaction, account must be taken of the fact that different forms of silicon have different effects upon the result. According to Berthelot, a gram atom of silicon on being converted into the hydrated dioxide evolves about 180 Calories of heat, whereas it will be seen later that the same weight of aluminium evolves only about 130 Calories. Thus the presence of this

[1] Hillebrand, United States Geological Survey, *Bulletin* 305.

silicon causes a larger heat of reaction than the same weight of aluminium. On the other hand, according to Ogier,[1] a gram molecule of hydrogen silicide evolves about 25 Calories when formed from hydrogen and crystalline silicon and 33 Calories when formed from amorphous silicon and hydrogen. When formed from aluminium silicide and hydrochloric acid, the heat of formation would doubtless be somewhat diminished. For the present purpose it is assumed to be about half the value given above, namely, 15 Calories. Making allowance for these facts, it is apparent that for the present purpose the total amount of impurity may be calculated as nearly equal to the amount of silicon found as such, namely, 0.28 per cent.

The sodium present was estimated as follows: 0.20 gram of the aluminium foil was dissolved in a platinum dish with pure hydrochloric acid, which gave no test for sodium in the spectroscope; the resulting solution was concentrated to about 1 milliliter and examined in the spectroscope. It was found to be about half as concentrated in sodium as a standard solution which contained 0.02 mg. per milliliter. This proves that the quantity of sodium present was less than 0.01 per cent. and may therefore be ignored.

To prepare the metal for use, it was polished on both sides with a mild abrasive; it was then carefully wiped with clean dry cotton and washed with ether to remove any film of grease which may have formed. It was then dried and cut into small pieces with a clean pair of shears.

The metal prepared in this way had a very bright surface and could not have been covered with a film of oxide of more than microscopic thickness. That a film of oxide existed, however, is shown by the fact that the pieces would not amalgamate when thrown on mercury, but if held below the surface of the mercury and scratched, amalgamation slowly occurred. No way was found to estimate the quantity of oxide actually present, because ordinary quantitative analysis could not detect an amount so small. Some idea of the probable quantity, however, may be obtained from the study of the oxidation of electrolytic zinc. The zinc exposed a much greater surface per unit of weight than the aluminium does, and should therefore be oxidized to a greater extent. Now the quantity of zinc oxidized was shown to be less than 0.04 per cent.; nevertheless, when it was thrown on dry mercury and stirred into it, little or no amalgamation took place. As soon as a solution of ammonia was added, however, amalgamation took place almost immediately, and very little zinc was found in the ammonia. It is thus evident that the coating of oxide which will prevent amalgamation is extremely thin; and there is accordingly little likelihood that the film of oxide covering

[1] Ogier, *Ann. chim. phys.* [5], **20**, 31, 1880.

the surface of the aluminium was great enough to introduce an appreciable error into the results. In view of these facts the aluminium was assumed to be 99.6 per cent. pure.

Magnesium.—Ribbon—the purest which could be obtained in the market—was used for this work. A careful analysis showed the presence of a small amount of iron and a trace of sodium.

The determination of the iron was made in the following manner: A weighed amount of the metal was dissolved in hydrochloric acid and sufficient ammonium chloride added to prevent the precipitation of magnesium hydroxide. While hot the solution was oxidized with chlorine, and the iron precipitated with ammonia twice in succession, and weighed as oxide. The results were as follows:

<div align="center">IRON IN PUREST COMMERCIAL MAGNESIUM.</div>

	Wt. of Mg.	Wt. of Fe_2O_3.	Equivalent wt. of iron.	Per cent. of iron.
1...................	2.50	0.0031	0.0021	0.08
2...................	2.86	0.0028	0.0020	0.071

Because the iron itself has some heat of solution (about 8 per cent. of that of an equal weight of magnesium), the fraction 0.075 per cent. would correspond to about 0.07 per cent. of inactive substance.

The sodium was estimated in the same manner as in the case of aluminium above and was found to be present in about the same quantity. Consequently, no correction for it was necessary.

To prepare the metal for use it was scraped with a knife in order to remove most of its coating of oxide, and afterwards polished with a mild abrasive, which was removed by rubbing with clean dry cotton. The metal then presented a very bright surface and could be kept in a stoppered weighing tube for a long time without tarnishing. There can be no doubt that the surface of the metal was still coated with a very thin film of oxide, because it would not amalgamate when held below the surface of mercury. In view of the experience with zinc, the weight of the oxide probably did not exceed 0.05 per cent. of the weight of the metal. Magnesium, like aluminium, is far more active than zinc, and therefore should be more easily oxidized; but the more compact form probably about compensated in the present case for the greater activity, because less surface was exposed with either aluminium or magnesium than with zinc.

As an outcome of these experiments, the magnesium was assumed to have a purity of 99.9 per cent. with an uncertainty probably not exceeding 0.05 per cent. in either direction.

Cadmium.—The cadmium used for this work was prepared electrolytically from cadmium sulphate which had been twice recrystallized from pure water, in precisely the same way as the zinc. The finely divided

crystals were washed with dilute ammonia solution until free from cadmium salt, then with water and finally with alcohol and ether, as before described, and were dried in a vacuum over concentrated sulphuric acid.

Since cadmium is a less active metal than zinc it should be less oxidized when prepared in the same manner. The quantity of zinc oxidized was found to be too small to introduce any serious error into the results. Therefore, the quantity of cadmium oxidized was not determined.

The mother liquor enclosed by the crystals of the metal was found to be considerable in amount; for its determination the method used in the case of zinc was employed.

VOLATILE MATERIAL ENCLOSED BY CRYSTALLIZED CADMIUM.

	Weight of cadmium.	Weight gained by drying tube.	Blank.	Weight volatile matter from cadmium.
1...............	5.00	0.00535	0.0001	0.00525
2...............	5.00	0.00510	0.0001	0.0050
3...............	5.00	0.0051	0.0001	0.0050
4...............	5.00	0.0048	0.0001	0.0047

Average, 0.00499

Since the electrolysis was conducted with a twenty-five per cent. solution, the corrected weight of mother liquor was 0.00665 gram; that is to say, the weight of enclosed mother liquor was 0.13 per cent. of the original weight of metal. The heat produced by the neutralization of this ammoniacal mother liquor was about one-sixth of the quantity which would be produced by the solution of an equal weight of cadmium; hence the correction to the weight for thermochemical purposes would be 0.11 per cent. As no other impurity was found in the cadmium, the metal was calculated as having a purity of 99.9 per cent.

Iron.—The iron used in this work was obtained from four different sources.[1] They will be spoken of as Samples A, B, C and D.

Sample A was iron reduced by hydrogen obtained from Kahlbaum and was undoubtedly very pure. It was prepared for use by being freshly reduced in hydrogen, at a very moderate temperature. Ignition at a very high temperature would have diminished the surface and therefore the speed of subsequent solution, by causing the particles to cohere more closely.

[1] A fifth sample was furnished by Professor C. F. Burgess, of the University of Wisconsin. It was prepared electrolytically and contained considerable hydrogen. The rate of solution is undoubtedly greatly influenced by the quantity of hydrogen present. When first obtained it dissolved at a rate comparable with the other samples. After having been kept for a year, however, it dissolved so slowly that no results could be obtained with it. The same effect was produced by heating it strongly in a vacuum for a considerable length of time. We wish to express our thanks to Professor Burgess for his courtesy in supplying this sample.

Sample B was similar in appearance; it was prepared from ferric nitrate which had been recrystallized four times from a strong nitric acid solution. The pure ferric nitrate had been heated in a platinum dish at a low temperature until converted to the dark red basic nitrate. This was then removed, finely ground,[1] and afterwards strongly heated in a platinum dish until completely converted to the oxide. The ferric oxide was placed in a porcelain boat and reduced at as low a temperature as possible in a current of pure hydrogen.[2]

Sample C was made by electrolysis of ferrous sulphate solution, to which had been added a small amount of ammonium chloride. The electrodes were of platinum, and, as soon as a thin layer of iron had formed, it was removed and kept under a dilute solution of hydrochloric acid. In this way thin plates of the metal were obtained, which exposed a considerable surface to the action of the acid. The preparation was finally washed with water and reduced in a current of hydrogen.

Sample D was prepared by the electrolysis of a solution of ferrous chloride. It was treated in the same manner as Sample C.

Of these samples, those reduced from pure oxide in hydrogen were undoubtedly the purest; these were essentially free from impurity. The electrolytic iron probably contained less than o . 1 per cent. of impurity derived from the electrolyte.

Apparatus.

The Calorimeter.—This work, involving the purest materials just described, was carried out with the aid of the adiabatic calorimeter, of which a vertical section is shown in the figure. The form of environment first employed consisted of two concentric cylindrical vessels of copper and a cover. The smaller cylinder, within which was placed the calorimeter proper, was secured inside of the larger one on legs made of hollow brass tubes about eight or ten centimeters in length. The space between the copper cylinders was filled with a solution of crude caustic soda, the liquid being allowed to come as near the top of the vessels as possible without danger of overflowing when stirred vigorously. The cover was a cylindrical vessel, also of copper, about ten centimeters in height, of such a diameter that it fitted easily inside the smaller cylinder, and projecting therein to such a depth that it was only two or three millimeters from the top of the calorimeter can. Four vertical brass tubes were soldered into the bottom of the cover, through which passed the stirrer, thermometer, and rod from which the basket containing the metal under treatment was suspended. The cover also was filled with

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[1] An iron mortar, according to Hempel, is obviously an ideal tool for this purpose.

[2] Richards and Baxter, *Proc. Am. Acad.*, 35, 253 (1900). *Z. anorg. Chem.*, 23, 245 (1900).

the crude alkaline solution, so that the calorimetric space was surrounded on all sides by an insulating layer of liquid about a decimeter thick, which could be kept by means of added acid so nearly at the same temperature as the calorimeter itself that the exchange of heat between them was negligible. The narrow annular space between the sides of the cover and the top of the inner cylinder was stopped by means of a rubber
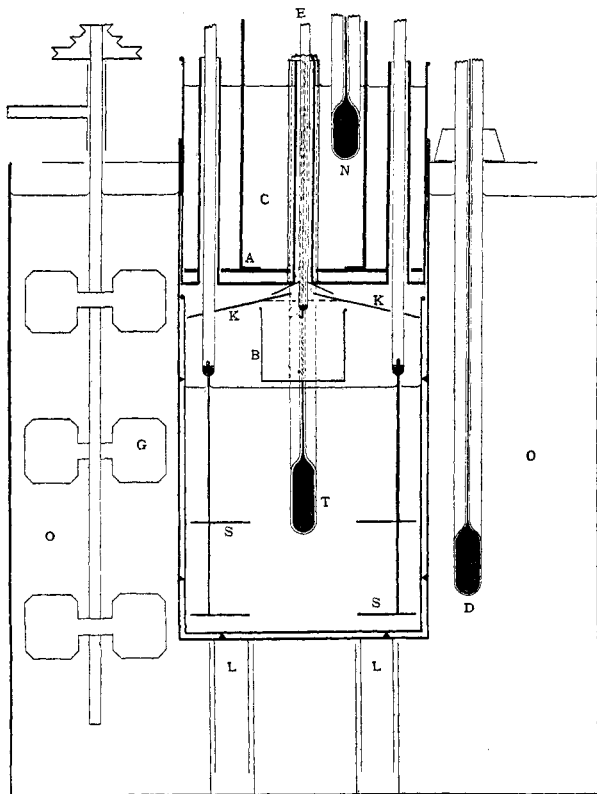

Fig. 1.

washer which was fastened to the sides of the cover. If this space was not closed, the current of air circulating through it was found to cause evaporation from the calorimetric vessel, and hence accidental cooling. The liquid in the large outside cylinder jacket was very vigorously stirred by means of a triple-screw propeller—a method which was found to be exceedingly efficient. The cover was stirred by means of a perforated copper disk which moved up and down at the same rate as the stirrer in the calorimeter proper. This method of stirring is not so efficient as the propeller, but was found to be adequate.

A few experiments at the close of the research were conducted by means of a modification of this calorimeter—a modification which on

the whole proved so satisfactory that it will be used in future work of this kind. This modification had already been used in principle in the work of Richards and Forbes in "Energy Changes Involved in the Dilution of Zinc and Cadmium Amalgams.[1] In this apparatus the cover of the environing bath was dispensed with, and the calorimeter proper was enclosed in a sealed can of metal wholly below the surface of the liquid in the large copper pail constituting the lower jacket. The tubes for the thermometer and other apparatus were attached to the lid of the sealed can, and the latter was wholly submerged. Thus the reaction was conducted in a sort of submarine vessel, having only a few tubes above the water level.

At first we feared that the cover would be difficult to make water-tight, and that the manipulation would be complicated by the firm attachment of the lid of the calorimeter can, but, as a matter of fact, these difficulties were found not to be prohibitory. By pressing a large flat elastic rubber washer between the top of the can and the lid, and holding the latter down by suitable clamp screws, a perfectly water-tight joint may be had, if the metal surfaces are smooth.

The best arrangement of these details has been described in a paper by R. H. Jesse, Jr., and one of us,[2] in whose investigation the apparatus was subjected to a much more thorough test.

A submerged vessel of this kind was found to provide altogether the best means of accomplishing the desired result. With this apparatus the experimenter has only one vessel to adjust at the temperature of the calorimeter inside, and the strain upon him is therefore distinctly less than when the lid also must be specially adjusted. The final results given by the calorimeter are exactly identical with those afforded by the other, as may be seen from the inspection of the results on zinc. The identity with the results obtained with the two sets of instruments is a valuable confirmation of each.

A cylindrical platinum can was used as the calorimeter proper. Its capacity was about 1.2 liters, and it weighed 177.25 grams. It was of such a size that it fitted loosely inside the inner copper cylinder of either form of adiabatic jacket, leaving an air space of about two or three millimeters in width on all sides. From the copper cylinder it was thermally insulated by means of triangular pieces of cork which were made as small as possible and placed with the apex against the calorimeter can. These pieces of cork were so small that their heat capacity was entirely negligible.

Thermometers.—Beckmann thermometers, graduated directly to hundredths and readily estimated to thousandths by means of a lens, were

[1] Carnegie Institution of Washington, *Publication* 56, 52 (1906).
[2] THIS JOURNAL, **32**, 268.

used for determining the temperature change of the calorimeter. They were very carefully standardized by comparison with two international standards, calibrated with the greatest care in Paris.[1] The comparisons were made while the Beckmann thermometers were subjected to precisely the conditions of exposed column, etc., to which they were submitted during the calorimetric determination, so that the corrections could be applied with strict consistency. The cruder thermometers used in the jacket and cover were graduated to twentieths and could be easily estimated to hundredths. They were compared with the standardized thermometers throughout the part of the scale used, and all were set so as to read together within two or three hundredths of a degree.

Stirrers.—In the early parts of the work a stirrer made from round glass rods bent and fused together was used inside of the calorimeter can. The surface exposed by such a system of rods is small, and consequently the stirrer would have to be driven at a high speed in order to produce very complete mixing. As will be shown later, this stirrer was not able, when running at a rate of about one hundred strokes per minute, to stir efficiently the calorimetric liquid. Accordingly, a stirrer made from sheet platinum and offering as great a surface as possible was used in all the final results. The diagram shows clearly the manner of its construction. It consisted of two rings, two centimeters in width, perforated with holes at regular intervals. These rings were connected by rods of platinum, which projected above the surface of the liquid. The rods were

Fig. 2.

sealed into glass tubes which passed through the cover and were connected to the driving mechanism.
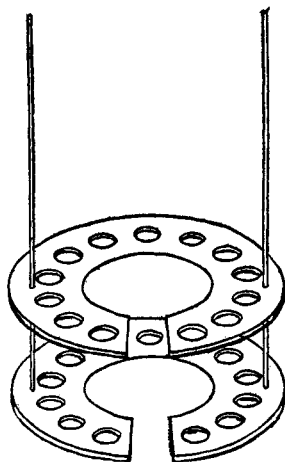
The Platinum Basket.—A cylindrical basket, about 4 cm. in diameter and 3 cm. high, made from platinum gauze, was used to support the metal to be dissolved. As the metal was sometimes very finely divided, it occasionally sifted through this gauze, and began to dissolve before its time. In order to prevent this cause of inaccuracy, a cap of platinum foil was sprung over the bottom of the basket outside, and just before the basket was lowered into the acid this cap was pushed off by means of a suitable device and allowed to fall to the bottom of the calorimeter. The basket itself was held by means of a stout hook of platinum wire, attached to the glass tube which ran through the copper tube attached to the center of the cover.

[1] These standards are described by Richards and Wells, *Proc. Am. Acad.*, **38,** 434 (1902); *Z. physik. Chem.*, **43,** 467 (1902).

Apparatus for Preventing Loss of Drops.—In the early experiments a considerable amount of the liquid, as much sometimes as one-half of a gram, was carried away in the form of drops by the escaping gas. These drops resulted, of course, from the bursting of the small bubbles as they rose to the surface. This is a familiar phenomenon whenever a gas escapes from a boiling or effervescing liquid. Several devices were tried to prevent this cause of inaccuracy. An inverted watch glass perforated in the center, placed over the top of the basket, served only partially to solve the difficulty. Next, a miniature bell-jar of very thin glass, fitting over the basket, and provided with a fine delivery tube above, just dipping under the liquid, was tested. This device collected the larger bubbles, but the smaller were driven throughout the liquid by means of the violent stirring and escaped from under the bell. Clearly some arrangement was necessary which should include in its scope practically all of the contents of the calorimeter, and, as a matter of fact, the difficulty
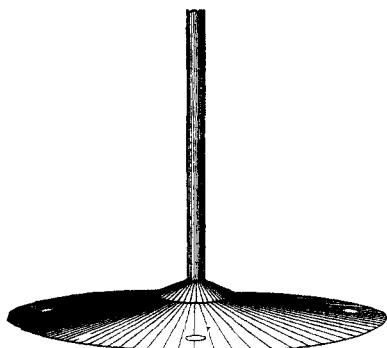

Fig. 3.

was entirely overcome by means of such an apparatus as is shown in the accompanying diagram. A large flat cone with a diameter almost as great as the internal diameter of the platinum calorimeter, and an altitude of not over 3 cm., was placed over the basket. At the apex a hole was cut to accommodate the rod which carried the basket. The cone was attached to the rod, leaving a space around it for the escape of the hydrogen, and a second small cone fitting closely to the rod was fastened a few millimeters above the first, in order to cover the opening provided for the escape of the gas. The fine bubbles of hydrogen slowly ran up the lower sides of the larger cone and collected in larger bubbles under the surface of the smaller cone, and from the edge of the smaller cone the gas bubbled through the liquid in a well-ordered manner, giving a minimum projection of the solution in the form of drops. As the heat capacity of the platinum cones was small and easily determined, this device introduced no error, and at the same time eliminated the difficulty in question. It was used in all the later experiments. Only Series 1, involving the solution of zinc, suffered from loss by the projection of drops, and to this a small correction was applied for the liquid which had escaped being warmed by the reaction in this fashion.

The Efficiency of Stirring.

It has been stated that previous work of others, as well as our own early experiments, were probably in error on account of inadequate

stirring.[1] The facts on which we base this statement will now be presented. In the experiments whose results are tabulated below, three different thermometers were used, all of which had been carefully standardized. No. 1 reached nearly to the bottom of the calorimeter, No. 2 about midway, and No. 3 only a short distance below the surface of the liquid. These three thermometers were used to measure the heat of solution of a definite amount of zinc in dilute hydrochloric acid. The heat capacity of the system was the same in each case and the same weight of metal was dissolved. The liquid was in each case stirred by the inadequate glass stirrer mentioned before. The corrected temperature rise as observed with the three thermometers is recorded in each case.

TEMPERATURE RISE AT DIFFERENT DEPTHS WITH INADEQUATE STIRRING.

Thermometer No. 1.	Thermometer No. 2.	Thermometer No. 3.
4.151	4.213	4.225
4.149	4.210	. . . . .
4.151	4.207	. . . . .
4.150	. . . . .	. . . . .
4.149	. . . . .	. . . . .
Mean, 4.150	4.210	4.225

The results with thermometer No. 2 are 1.45 per cent. and that with No. 3 1.8 per cent. higher than those with No. 1; that is to say, the liquid at the top remained consistently warmer than that at the bottom during the experiment, which is exactly what would be expected if the stirring were inefficient. When the thermometer bulb was at the bottom, the temperature indicated by it was undoubtedly too low throughout the whole progress of the experiment. This caused the jacket to be kept at too low a temperature and the reacting system must have lost heat to the surroundings. A parallel error would have come from this cause if the Regnault-Pfaundler method had been used to compute the cooling correction, and has probably entered into much similar work in the past.

After the discovery of this unexpected source of error, the glass stirrer was entirely rejected, and the far more efficient stirrer of platinum alone was used. Experiments were then instituted to discover how rapidly this must be operated in order to commingle adequately the reacting substances. Forty strokes per minute still left an error of over 0.2 per cent., while sixty strokes per minute gave adequate mixing, as judged from the constancy of the outcome. This may be given here, as a contrast to the results in the preceding table. The following results were obtained with two different rates of stirring and two different thermometers. The first thermometer reached about midway, and the second nearly to the bottom of the calorimeter. The heat generated by stirring was

[1] W. P. White has independently come to the same conclusion, *Phys. Rev.* (1908).

determined and in each case the appropriate correction was applied. The values for this correction will be given later. In each case 7.500 grams of zinc were dissolved in 941.4 grams of dilute acid. The nine experiments are arranged below in two ways—first classified as to speed of stirring (Series I and II) and then classified according to the thermometer used (Series III and IV).

TEMPERATURE RISE AT DIFFERENT DEPTHS WITH ADEQUATE STIRRING.

Series I. 110 strokes per minute.	Series II. 60 strokes per minute.	Series III. Thermometer 1.	Series IV. Thermometer 2.
4.247°	4.246°	4.247°	4.244°
4.245°	4.245°	4.245°	4.247°
4.244°	....	4.246°	4.246°
4.246°	....	4.247°	....
4.247°	....	4.246°	....
4.246°	....	4.245°	....
4.247°	....	....	....
Aver., 4.2460°	4.2455°	4.2460°	4.2457°

These results prove conclusively that with the rates of stirring employed the mixing was very complete and the liquid was uniformly warmed throughout the reaction, for the differences between each average and the general average are of the same order as the probable error of each. In other words, the results are identical within the limits of experimentation. Hence the rate of sixty strokes per minute was adequate, with our efficient stirrer, to accomplish the desired result.

Correction for Heat Evolved by Stirring.

The rate of stirring required for these experiments was sufficient to cause considerable heat to be generated. This quantity must obviously be determined for each liquid used. In the adiabatic calorimeter the determination may be made with great ease and precision.

When the acid solution ($HCl.20H_2O$) was stirred at the highest rate employed, i. e., 110 strokes per minute, the following results were obtained:

	Time. Min.	Temperature rise.	Average rise per minute.
1............................	20	0.025°	0.00124°
2............................	15	0.018°	0.00120°
3............................	30	0.038°	0.00125°
Total...................	65	0.081°	0.00123°

When the more concentrated acid ($HCl.8.808H_2O$) was stirred at the same rate, a rise of 0.054° was caused in 30 minutes, at the rate of 0.0018° per minute. Thus the denser liquid caused a greater stirring correction, partly because of its lower heat capacity.

With the same acids and the slower rate of stirring (60 strokes per minute) the correction assumed the following much smaller values:

Acid.	Time. Min.	Temperature rise.	Average rise per minute.
HCl.8.808H$_2$O..............	60	0.009°	0.00015°
HCl.20H$_2$O................	40	0.006°	0.00014°
HCl.20H$_2$O................	60	0.008°	0.00014°

The value for the least concentrated acid (HCl.200H$_2$O) was not determined, but since the heat capacity of the system in that case was about 10 per cent. greater than that with the acid (HCl.20H$_2$O) the stirring correction was undoubtedly about 0.007° in an hour. It is interesting to note that when the rate of stirring is doubled the heat generated is increased about tenfold. This is in approximate agreement with experience of naval engineers in calculating the quantity of coal necessary to drive ships at sea.

Possible Error Caused by Heat Exchange with Surroundings.

If the environment of the calorimeter is kept *exactly* at the temperature of the calorimeter, no heat exchange can take place. Since perfect exactness in this adjustment is not often to be attained, we investigated with care the possible effect of slight imperfections in the adjustments of temperatures. We had expected to find nearly equal effect in the two opposite directions of cooling and warming, but somewhat to our surprise, this expectation was not fulfilled. When the temperature of the jacket was maintained 0.1° higher than that inside the calorimeter for a period of twenty minutes, only a barely appreciable change was observed in the temperature inside the calorimeter; but when it was 0.1° lower a very noticeable cooling effect is manifested. This latter effect was probably due to a distillation of the water out from the calorimeter and subsequent condensation on the copper walls of the inside of the jacket. Distillation into the calorimeter when the outside jacket was warmer could not take place, because the calorimeter space is entirely protected from the outside air, and there was then no source of moisture to draw upon. It is possible that evaporation into the slight current of air drawn through the tubes also contributed to the effect.

This observation, which was first made by one of us in collaboration with Dr. A. W. Rowe, is so important in its bearing upon calorimetric work in general that a typical series of results should be given. In the first place, the outer jacket was adjusted at precisely the same temperature as the calorimeter, and the small correction for the stirring of the latter was noted. The jacket was then kept at a temperature just 0.1° above the calorimeter, and the further progress of the temperature was carefully observed. Two rates of stirring were employed in two different experiments, one very active, and the other somewhat less so. Having thus determined the effect of having the jacket too hot, the same experiment was repeated with the opposite disturbing cause—the jacket

around the calorimeter was kept 0.1° too cool. The results are recorded in the table below; in each case the test lasted forty minutes:

EFFECT OF MAINTAINING JACKET AT TOO HIGH OR TOO LOW A TEMPERATURE.

Rate of stirring.	Correction for stirring for time named.	Excess of jacket temperature.	Change in calorimetric temperature.	Effect to be measured.
Rapid............	0.006°	+0.1°	+0.008°	+0.002°
Slow............	0.002°	+0.1°	+0.004°	+0.002°
Rapid............	0.006°	—0.1°	—0.018°	—0.024°
Slow............	0.002°	—0.1°	—0.021°	—0.023°

Thus each set of experiments is entirely consistent within itself; clearly, the exposure of the calorimeter to an environment warmer by 0.1° only alters the temperature of the former by 0.001° in twenty minutes; but if the difference of temperature is in the opposite direction, the cooling correction is more than ten times as great.

These experiments demonstrate the faultiness of Rumford's method of correcting for cooling by starting a reaction as much below the temperature of the room as the process concludes above it. Evidently, if the calorimeter is in a closed metal vessel like ours, the gain in heat during the first part of the process will be only about one-tenth as great as the loss during the latter part, and the total observed evolution of heat will be much too small. Because Rumford's method has usually been used in the case of the solution of metals in acids, the discovery of this source of error is especially pertinent to the present work.

After the discovery of these circumstances the temperature in the jacket is always kept one or two hundredths of a degree above rather than a little below that in the calorimeter. There was no difficulty in keeping the temperature of the jacket within 0.1° of that of the calorimeter throughout an experiment, and for the greater part of the time the difference was 0.05° or less, hence it is evident that no error is introduced in the present case from this source. The stirring correction was determined under precisely similar conditions, and hence could be consistently applied.

Correction for Evaporation of Acid.

The hydrogen evolved during these reactions is saturated with the vapor of the solution in which it is produced. Others have considered it as saturated with aqueous vapor only, and the correction has been calculated, assuming that the heat of evaporation of water was the same from an acid solution as from pure water. We thought it worth while to test this assumption by experiment, and the following account of the test may well be given here following that of the other small corrections, although the application of the results is not in place until the completion of the chief part of the experiment.

The test was conducted by bubbling dry air through the usual amounts

of the various solutions concerned, kept at the average temperature of the main experiment, and noting the fall of temperature actually produced per liter of air.[1]

The details of experimentation were as follows: Into an eight-liter roughly graduated bottle was run a stream of water, thus forcing the imprisoned air through the driers, which consisted of two sulphuric acid wash bottles and a phosphorus pentoxide tube. The air subsequently passed through a long coil of lead pipe in the calorimeter and a shorter coil in the cover, to ensure that the air should be at the same temperature as the liquid inside. It then passed through a central tube of the cover and bubbled through the liquid inside the calorimeter. In order to prevent the absorption or emission of an appreciable amount of heat by the air in passing through that very small part of the tube exposed to the air of the room, the latter was kept as near the temperature of the experiment as possible.

A thermometer was placed in the bottle to measure the temperature of the air at the beginning of the experiment, and a mercury gauge also was inserted to indicate the difference in pressure. The volume of the air was corrected to standard conditions. In order to test the accuracy

	Liquid.	Heat capacity of system in Calorie units.	Initial temp. of exp.	Corrected volume of air in liters.	Observed fall of temperature.	Correction for heat by stirring.	Corrected fall.	Average per liter.
1	Pure water ...	913	18.0°	6.62	—0.063°	—0.005°	—0.068°	—0.0101°
2	" ...	913	18.0°	7.40	—0.074°	—0.005°	—0.079°	—0.0105°
							Mean,	—0.0103°
3 1	HCl.200H$_2$O ..	900	17.6°	7.60	—0.074°	—0.005°	—0.079°	—0.0105°
4 2	" ..	900	18.0°	7.47	—0.076°	—0.005°	—0.081°	—0.0107°
5 3	" ..	900	18.0°	7.42	—0.073°	—0.005°	—0.078°	—0.0105°
							Mean,	—0.0106°
4	HCl.20H$_2$O ...	814	18.0°	7.47	—0.082°	—0.006°	—0.088°	—0.0117°
5	" ...	814	17.9°	7.48	—0.083°	—0.004°	—0.087°	—0.0116°
6	" ...	814	17.7°	7.56	—0.085°	—0.005°	—0.090°	—0.0118°
							Mean,	—0.0117°
7	HCl.8.8H$_2$O ..	732	18.0°	7.41	—0.048°	—0.006°	—0.054°	—0.0073°
8	" ..	732	18.1°	7.38	—0.053°	—0.005°	—0.058°	—0.0077°
							Mean,	—0.0076°

[1] Dry hydrogen would perhaps have been better, but we assumed that the same quantity would evaporate into each gas.

of the method, pure water was at first experimented upon, and the results are given in the table above, with those concerning the acid. The table explains itself; attention is called to the fact that the last column contains the essential outcome of the experiment, namely the cooling effect produced on the given calorimetric system by evaporation into a single liter of dry gas. The mean temperature of the other experiment (18°) was chosen for these experiments.

Evidently the cooling effect produced in pure water and the two most dilute solutions of hydrochloric acid is almost the same, allowing for the somewhat different heat capacities of the two systems, as indeed one would expect; but with the most concentrated acid the cooling effect is very much less in proportion. On comparing the actually observed cooling effects with those calculated from the tension and latent heat of pure aqueous vapor at the appropriate temperatures (0.0098°, 0.0099°, 0.0109° and 0.0121°, respectively), it is apparent that in every case except the last the method gives a higher result than the theoretical one by an amount averaging about 5 per cent. This is undoubtedly in part due to the cooling effect produced by the expansion of the gas, as it rises through the liquid, but this effect is not large enough to account for the whole difference. The discovery of the cause of irregularity would have constituted a research in itself, and as an accuracy of 5 per cent. was enough for our present purpose, the matter was not followed further at this time. The diminished cooling effect in the most concentrated acid is the important outcome of this series of experiments.

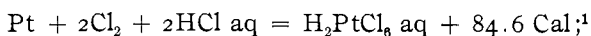### The Heat of Solution of Metals in Concentrated Acids.

The heats of solution of the metals, zinc, aluminium, magnesium, cadmium, and iron have all been determined in the course of the present research, and so also have the heats of dilution of the liquid factors and products concerned, in order that all the results might be reduced to the usual dilution with 200 molecules of water. The present section deals with the determination of the heat of solution.

In each case (except a few of the experiments with magnesium) enough metal was used to cause in the calorimetric system employed in its particular case, a change of temperature of about 4°, and in each case the final temperature was not far from 20°, the range being from the neighborhood of 16° to that of 20°. Because of the widely different speeds of reaction with these five different metals, different concentrations of acid were needed in the different cases in order that the reaction should neither be too rapid nor too slow in rate. For zinc and aluminium the concentration $HCl.20.0H_2O$ was used; for the magnesium a solution in ten times as much water ($HCl.199.8H_2O$); and for cadmium and iron, which dissolved much more slowly, the far more concentrated solution, $HCl.8.808H_2O$ was needed, and even this acted with extreme slowness.
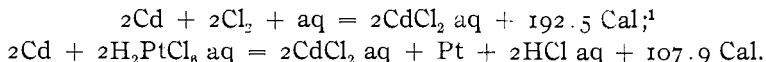
Stronger solutions were not used because of the large amount of acid which evaporates from them, and because of the excessive complication introduced by the great heat of dilution. Hydrochloric acid was used rather than sulphuric because there is no danger in the case of hydrochloric acid of the existence of such side reactions as are caused by the partial reduction of sulphuric acid.

The method of experiment was essentially the same in the case of each metal. A weighed quantity of acid was placed in the calorimeter and a weighed quantity of metal in the basket. The whole apparatus was then assembled in the manner shown in the diagram (Fig. 1). The temperature of the jacket and cover were adjusted to that of the calorimeter, and the whole was allowed to stand for ten or fifteen minutes to make sure that the basket and metal had reached the temperature of their surroundings. The stirrers were put in motion, and the thermometer was read until a constant reading was obtained for several minutes. The basket was then lowered into the acid and the rise of temperature inside equaled in the jacket by running concentrated sulphuric acid from the burettes. These burettes were graduated in tenths of a degree—that is to say, they indicated the amount of acid necessary to raise the alkaline solution in the jacket by successive increments one-tenth of one degree. The reaction of course became slower and slower, as it proceeded, and finally, when the temperature rise settled down to the regular rise due to the known correction for the stirring, the reaction was known to be at an end, and the final temperature readings were made.

As will be seen from the table below, the time necessary varied greatly in the different cases, depending in part upon the accidental arrangement of the pieces of metals in the basket and in part upon their chemical nature. In the cases of cadmium and iron, the reactions were so deliberate that it was necessary to introduce platinum chloride into the solution in order to catalyze the reaction. This resulted, of course, in a side reaction, involving the deposition of a small amount of platinum and the corresponding evolution of slightly too much heat. The platinum so deposited was collected by filtration and was weighed at the close of the experiment. The correction was applied duly in each case, and amounted on the average to somewhat less than four one-thousandths of a degree in the case of iron, the average amount of platinum precipitated in each case being about 8 milligrams in the case of cadmium and 10 milligrams in the case of iron. The equations necessary for calculating the reaction for the platinum precipitated by cadmium are as follows:
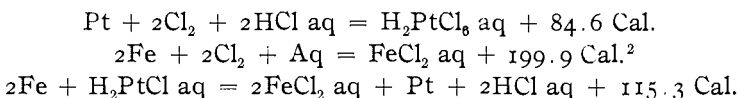
$$Pt + 2Cl_2 + 2HCl \text{ aq} = H_2PtCl_6 \text{ aq} + 84.6 \text{ Cal};[1]$$

[1] Thomsen, *Thermochemische Untersuchungen,* 3, 431 (1883).

$$2Cd + 2Cl_2 + aq = 2CdCl_2 \, aq + 192.5 \, Cal;[1]$$
$$2Cd + 2H_2PtCl_6 \, aq = 2CdCl_2 \, aq + Pt + 2HCl \, aq + 107.9 \, Cal.$$

By subtracting from this the value for the reaction $2Cd + 4HCl \, aq = 2CdCl_2 \, aq + 2H_2 + 35.0 \, Cal.$, we obtain the quantity of heat which is introduced by the action of one gram-atom of platinum, *i. e.*, 73 Cal. The correction was calculated by means of the following formula:

$\beta = 73 \times W/M \times K$, where β = correction in thousandths of one degree, W = weight of platinum found, M = atomic weight of platinum, and K = heat capacity of system.

The equations used in calculating the correction for platinum precipitated by iron are as follows:

$$Pt + 2Cl_2 + 2HCl \, aq = H_2PtCl_6 \, aq + 84.6 \, Cal.$$
$$2Fe + 2Cl_2 + Aq = FeCl_2 \, aq + 199.9 \, Cal.[2]$$
$$2Fe + H_2PtCl \, aq = 2FeCl_2 \, aq + Pt + 2HCl \, aq + 115.3 \, Cal.$$

Subtracting from this the heat of solution of two gram-atoms of iron:

$$2Fe + 4HCl \, aq = 2FeCl_2 \, aq + 2H_2 + 42,$$
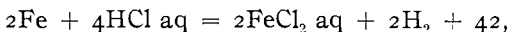
gives the output of heat (73 Cal.) for one gram-atom of platinum. The correction is calculated by means of the equation already given, the evolution of heat being essentially identical in the two cases. A portion of the liquid was removed with a pipette immediately at the close of the experiment and tested with sulphocyanate; no trace of oxidation was observed.

The heat capacities of the various factors in the reaction, including the calorimetric apparatus which was warmed by it, were computed from the weights of the several parts. By far the most important portion of the heat capacity consists of the acid solution, and accordingly, especially accurate determinations were needed. We are greatly indebted to Dr. A. W. Rowe for his kindness in determining the specific heats of the three acids used by us between the temperatures of 16° and 20°, by the new method now in use in Harvard University.[3] The specific heats of the three acids employed were respectively as follows: the weakest solution ($HCl.199.8H_2O$) 0.9814, the solution of medium concentration ($HCl.20.0H_2O$) 0.8486, the most concentrated solution ($HCl.8.808H_2O$), 0.7312, compared with water over the same range, 16 to 20°. The specific heats of the various pieces of apparatus (with the exception of the thermometer) and the metal dissolved are given with sufficient accuracy by previous determinations made by others and were taken as follows:

[1] Thomsen, *Thermochemische Untersuchungen*, 3, 284 (1883). For the sake of consistency Thomsen's somewhat crude figures were used throughout.

[2] *Ibid.*, 3, 287.

[3] Richards and Rowe, *Proc. Am. Acad.*, 43, 475 (1908); *Z. physik. Chem.*, 64, 187 (1908).

Zn................... 0.098		Fe.................... 0.112	
Al.................... 0.202		Pt.................... 0.032	
Mg................... 0.245		Glass................. 0.186	
Cd................... 0.054			

The thermometer was estimated by the method given in Ostwald-Luther's well-known "Handbuch."[1] The following table gives the heat capacities of the various systems concerned. The two series of experiments with zinc differ only in that the first series was conducted with the inadequate glass bell for preventing the projection of drops of liquid. Accordingly the specific heat of 25 grams of glass had to be included in the system, and a correction of one-quarter of a gram had to be made for the liquid lost by projected drops of liquid. The amount of this loss was found to be on the average about one-half a gram, and one-half of this quantity was taken, because the loss was gradual from the beginning to the end of the experiment. In the second series with zinc and all the other series with other metals the platinum cone, weighing about 9 grams, replaced the inadequate glass bell, and no important amount of acid was lost by the projection of drops. The differences in the heat capacities of the acids are due to the different specific heats and weights taken. The system included also half of the air in the space surrounding the calorimeter by means of which the latter was insulated from the inner cylinder of the jacket. The volume of air was calculated to be 160 cubic centimeters, which at constant pressure has a heat capacity of 0.22 mayer. Since the total heat capacity of the system was always over 3000 mayers, this quantity may safely be neglected, as being beyond the accuracy of the measurement.

In the first three experiments with zinc, 941.2 grams of acid were used; in each of the other experiments with zinc and aluminium the weight of acid was 941.4 grams. In the case of magnesium, 904.0 grams of the more dilute acid were employed, while the most concentrated acid used in the experiments with cadmium and iron, weighed 983.0 grams in each trial. Here is given a table showing the heat capacities of the several systems, calculated from the foregoing data.

	First zinc.	Second zinc.	Aluminium.	Magnesium.	Cadmium.	Iron.
Platinum.............	8.4	8.7	8.7	8.7	8.7	8.7
Glass................	4.7	...	...	...	...	...
Acid.................	798.7	798.9	798.9	887.2	718.8	718.8
Metal................	0.7	0.7	0.2	0.2	0.8	1.0
Thermometer.........	1.4	1.4	1.4	1.4	1.4	1.4
Total in Cal/$t°$	813.9	809.7	809.2	897.5	729.7	729.9
Total in mayers.......	3404.	3386.	3384. ·	3753.	3053.	3053.

[1] Ostwald-Luther, "Hand- und Hülfsbuch zur Ausführung physikochemischer Messungen," 2nd edition (1902).

With successive preparations of each of these systems a number of experiments on the heat of solution of metals in acids were made. More experiments were made with zinc than with the other elements for three reasons: in the first place because the first method which had been used was not wholly satisfactory, in the next place because experience was at that time being gained concerning all the details of the manipulation, and finally because two entirely different samples of zinc were tested.

The volume of hydrogen evolved in each of these experiments under standard conditions was calculated, and multiplied by the average fall in temperature per liter of gas passed through each calorimeter full of each acid, according to the table already given on page 451.

A sample experiment showing the general method is given below.

The Heat of Solution of Zinc.

7.5 grams of electrolytic zinc were used, being equivalent, according to the analysis, to 7.496 grams of pure zinc. The calorimeter contained 941.4 grams of acid or 2.372 moles of hydrogen chloride. The temperature of the air was 18°. This is the experiment number 6 below.

Time.	Reading of thermometer in calorimeter.	Reading of thermometer in the jacket reduced to the same standard as the calorimeter.	Reading of the thermometer in the calorimeter corrected for errors of calibration.
0	0.830	0.82	0.808
1	0.830	0.82	0.808
2	0.830	0.85	0.808
3	0.830	0.85	0.808
20	5.010	5.02	5.027
22	5.031	5.04	5.049
23	5.033	5.08	5.051
24	5.035	5.09	5.053
25	5.035	5.05	5.053
26	5.035	5.05	5.05
27	5.036	5.04	5.054
28	5.036	5.02	5.054

Thus the difference between the corrected readings of the thermometer was 4.246. To this must be added 0.002° for the correction for the thread of the thermometer exposed to the somewhat cooler air of the room, and from the results must be subtracted 0.003° for the heat added by the stirring, the slower rate having been used in this experiment. The final temperature attained was 19.87°. The volume of hydrogen evolved, reduced to standard conditions, was 2.57 liters, which number being multiplied by the cooling effect of one liter of gas under the same conditions (0.0117°), gives 0.030°, the correction to be applied for the vaporization of the solution. The corrected rise of temperature is 4.275° in a heat capacity of 809.7. Multiplying these two quantities together, the heat evolved in the experiment, expressed in 18°-Calories, is found to be 3461 Calories. A table containing the data for all the metals follows:

DATA CONCERNING THE HEAT OF SOLUTION OF FIVE METALS IN HYDROCHLORIC ACID AT 20°.

No. of exp.	Designation.	Corr. weight of pure metal, Gms.	No. of moles of HCl in calorimeter.	Duration of exp.	Corr. change of thermometer reading.	Corr. for heat by stirring.	Corr. for solvent vaporized by hydrogen.	Corrected rise of temperature.	Heat capacity of system in Cal/T_0.	Heat evolved in experiment (in 18° calories).
1	Zn (A)..........	7.496	2.372	37	4.268°	—0.046°	+0.030°	4.252°	813.9	3461
2		7.496	2.372	20	4.245°	—0.025°	+0.030°	4.250°	813.9	3459
3		7.496	2.372	24	4.248°	—0.029°	+0.030°	4.249°	813.9	3458
4		7.496	2.372	17	4.268°	—0.021°	+0.030°	4.277°	809.7	3463
5		7.496	2.372	12	4.260°	—0.014°	+0.030°	4.276°	809.7	3462
6		7.496	2.372	25	4.248°	—0.003°	+0.030°	4.275°	809.7	3461
									Average,	3461
7	Zn (B)..........	7.500	2.372	18	4.269°	—0.022°	+0.030°	4.277°	809.7	3463
8		7.500	2.372	16	4.267°	—0.020°	+0.030°	4.277°	809.7	3463
9		7.500	2.372	15	4.249°	—0.002°	+0.030°	4.277°	809.7	3463
10[1]		7.500	2.372	22	4.249°	—0.003°	+0.030°	4.276°	809.7	3462
									Average,	3463
11	Al..............	0.747	2.372	55	4.296°	—0.008°	+0.008°	4.296°	809.2	3475
12		0.747	2.372	23	4.287°	—0.003°	+0.008°	4.292°	809.2	3473
13		0.747	2.372	20	4.289°	—0.003°	+0.008°	4.294°	809.2	3475
14		0.747	2.372	26	4.287°	—0.004°	+0.008°	4.291°	809.2	3472
15		0.747	2.372	25	4.288°	—0.004°	+0.008°	4.292°	809.2	3473
16		0.747	2.372	23	4.291°	0.003°	+0.008°	4.296°	809.2	3475
									Average,	3474

[1] This experiment was performed with the submarine apparatus; all others with the original form of calorimeter.

Data Concerning the Heat of Solution of Five Metals in Hydrochloric Acid at 20° C—(*Continued*).

No. of exp.	Designation.	Corr. weight of pure metal. Gms.	No. of moles of HCl in calorimeter.	Duration of exp.	Corr. change of thermometer reading.	Corr. for heat by stirring.	Corr. for solvent vaporized by hydrogen.	Corrected rise of temperature.	Heat capacity of system in Cal/T°.	Heat evolved in experiment (in 18° calories).
17	Mg..............	0.8492		22	4.283°	—0.003°	+0.008°	4.288°	897.5	3848
18		0.8492		22	4.278°	—0.002°	+0.008°	4.284°	897.5	3845
19		0.8492		23	4.279°	—0.002°	+0.008°	4.285°	897.5	3846
20		0.4246		20	2.140°	—0.002°	+0.004°	2.142°	897.4	1922
21		0.4246		21	2.141°	—0.002°	+0.004°	2.143°	897.4	1923
22		0.4246		24	2.143°	—0.002°	+0.004°	2.145°	897.4	1925
	Average,	0.8492							Average,	3846
23	Cd..............	14.983	5.038	29	3.594°	—0.009°	+0.022°	3.607°	729.7	2632
24		14.983	5.038	49	3.604°	—0.012°	+0.022°	3.614°	729.7	2637
25		14.983	5.038	51	3.594°	—0.006°	+0.022°	3.610°	729.7	2634
26		14.983	5.038	41	3.664°	—0.077°	+0.022°	3.609°	729.7	2634
27		14.983	5.038	21	3.632°	—0.040°	+0.022°	3.614°	729.7	2637
									Average,	2635
28	Fe, A...........	9.000	5.037	94	4.530°	—0.019°	+0.027°	4.538°	729.9	3312
29	A...........	9.000	5.037	166	4.533°	—0.026°	+0.027°	4.534°	729.9	3309
30	B...........	9.000	5.037	97	4.528°	—0.018°	+0.027°	4.537°	729.9	3312
31	B...........	9.000	5.037	43	4.513°	—0.005°	+0.027°	4.535°	729.9	3310
32	C...........	9.000	5.037	109	4.538°	—0.025°	+0.027°	4.540°	729.9	3314
33	D...........	9.000	5.037	235	4.553°	—0.040°	+0.027°	4.540°	729.9	3314
									Average,	3312

The table explains itself, the five metals, zinc, aluminium, magnesium, cadmium, and iron being named in the order in which they were investigated in the second column, and the various essential data concerning the several experiments being given in the following columns. The last column of all contains the products of the several parts of numbers in the two preceding columns and gives the various amounts of heat evolved in each of the several experiments. These values are those which would be manifested by an isothermal reaction conducted at the final temperature attained in each case, $20°\pm$, because the heat capacities of the factors were used in calculating the results.[1]

Comparison of the results in the last column of this table shows that the calorimetric method had been brought to a high degree of constancy, because the agreement between the several results for each reaction is excellent; that is to say, the probable error of each of these averages is small, in so far as the actual errors of experimentation are concerned. Except in the case of cadmium, which is the least satisfactory, the maximum difference from the mean of the individual determinations is very little over one-twentieth of one per cent., and even in the case of cadmium it is only about one-tenth of one per cent. The probable error calculated according to the method of least squares is accordingly much less than this. Evidently we have here a list of data far more accurate than anything of the kind which has been published before. For example, Thomsen's results for zinc, with which he made more experiments than in the other cases, vary from 34.04 to 34.69 Calories—an extreme variation of nearly 2 per cent., or a deviation from the mean of about 1 per cent. on each side. This is a grade of accuracy over tenfold less than that shown by the present series of determinations. The average final results are brought together in the following table, together with the same calculated upon the basis of a gram-atom of metal instead of the small amount which happened to be used in the experiment. The latter are given both in terms of large Calories ($18°$) and kilojoules, the factor 4.182 being employed for the computation of kilojoules. The range over which the specific heats were measured being $16-20°$, the Calorie is taken at $18°$.

HEAT OF SOLUTION OF THE METALS IN AN EXCESS OF HYDROCHLORIC ACID AT $20°$.

Metal.	Concentration of acid.	Weight of metal dissolved.	Heat evolved in experiment (in small Calories).	Atomic weights.	Heat evolved for 1 gram-atom of metal.	
					In large Calories ($20°$).	In kilojoules.
Zn +	$HCl.20H_2O$	7.496	3462	65.37	30.19	126.8
Al +	$HCl.20H_2O$	0.7470	3474	27.1	126.0	527
Mg +	$HCl.200H_2O$	0.8492	3846	24.32	110.15	460.6
Cd +	$HCl.8.8H_2O$	14.985	2635	112.42	19.77	82.68
Fe +	$HCl.8.8H_2O$	9.000	3312	55.85	20.55	85.94

[1] Richards, THIS JOURNAL, **25,** 209 (1903).

The direct comparison of these numerical values with Thomsen's is not immediately possible, because in all cases the acid used by us was of a different concentration from that used by him. It has already been shown that Thomsen's method of calculating for more dilute acids was erroneous, so that only his actual uncorrected results with acids more concentrated than $HCl.200H_2O$ are worthy of consideration.

An essential part of the research, without which the results recounted in the present paper are incomplete, is therefore the precise determination of the heats of dilution of the several acid solutions concerned. This work has already been almost finished, awaiting only a few final determinations for completion. The details will soon follow in a second paper.

Summary.

1. The new method of adiabatic calorimetry was applied to the solutions of metals in acids. The method is particularly adapted to the determination of the energy change involved in these reactions on account of the length of time required by them.

2. The faults in the old method of estimating the weight of metal dissolved are pointed out and a method of avoiding them is described.

3. It has been shown that in order to insure the complete equality of temperature during the reaction, the stirring within the calorimeter must be very vigorous. All the previous results are probably in error from lack of this knowledge.

4. The quantity of heat generated by stirring a liquid is shown to be increased nearly 10 times when the rate of stirring is doubled.

5. The cooling effect of the evaporation of the acid solution into the escaping hydrogen has been directly evaluated and a suitable correction applied.

6. The quantity of oxide on the surface of the metals employed was shown to be extremely small, and the purity of the materials was carefully investigated, suitable corrections being applied when necessary.

7. The heats of solution of the metals zinc, aluminium, magnesium, cadmium, and iron in hydrochloric acid were determined.

8. The error in Thomsen's method of calculating the heat of solution of a metal in dilute acid from the data obtained with concentrated acid is pointed out.

9. The second part of this paper, containing the essential heats of dilution concerned, will follow soon.

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