the possibility of a change of attraction with temperature was further especially considered in a paper on chemical energy,[1] and no evidence whatever for such a belief was found in the case investigated.

Summary.

1. The relation proposed by Whittaker that "The surface energy of a liquid in contact with its own vapor at any temperature is proportional to the product of the internal latent heat and the (absolute) temperature" has been investigated and the conclusion drawn that the relation is only approximately true.

2. The relation is shown to suggest a division of the so-called surface energy of a liquid into two parts, one part due to the liquid surface and the other to the surface of the vapor over the liquid. Further investigation of this suggestion is promised.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

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

PART II. THE HEAT OF DILUTION OF THE ACID SOLUTIONS.

BY THEODORE W. RICHARDS, ALLEN W. ROWE AND L. L. BURGESS.

Received July 8, 1910.

Introduction.

An account of a new series of determinations of the heat of solution of five metals in fairly concentrated acids was published in a recent number of THIS JOURNAL.[2] There it was shown that the heats of dilution, both of the acids and of the residual solutions after the reactions had been completed, affect the result much more than has usually been supposed. It was made clear that the actual results of the heats of solution of the metals in fairly concentrated acids must receive large corrections in order that they may all be reduced to the common standard of the heat of solution of the metal in the theoretical amount of acid of the standard dilution $HCl.200H_2O$. The actual attainment in a single experiment of this theoretical result is not possible because the completion of the reaction of the theoretical quantities would require an exceedingly long time, and therefore could not be measured with precision in the calorimeter.

As an example of the correction of the results, the case of zinc may be cited. In a single experiment 7.496 grams of pure zinc were dissolved in 941.4 grams of acid of the concentration $HCl.20H_2O$, and in the process 3461.0 calories of heat were evolved. This amount of zinc is 0.11467 gram atom, and the solution actually in the calorimeter contained 2.372

---

[1] *Trans. Am. Electrochem. Soc.*, 14, 35 (1908).

[2] Richards and Burgess, THIS JOURNAL, 32, 431 (1910).

gram molecules of hydrogen chloride. Accordingly the actual reaction in the calorimeter was as follows:

$$0.11467\ \text{Zn} + 2.372\ (\text{HCl}.20\text{H}_2\text{O}) = 0.11467\ \text{H}_2 + (0.11467\ \text{ZnCl}_2 + 2.143\ \text{HCl} + 47.44\ \text{H}_2\text{O}) + 3461\ \text{calories}.$$

On multiplying this equation by 8.721 in order to find the amount of heat evolved by the solution of 1 gram atom of the metal, the following equation is obtained:

$$\text{Zn} + (20.69\ \text{HCl} + 414\ \text{H}_2\text{O}) = \text{H}_2 + (\text{ZnCl}_2 + 18.69\ \text{HCl} + 414\ \text{H}_2\text{O})$$
$$(x = 30183\ \text{calories or}\ 126.8\ \text{kilojoules}).$$

Thus a very large excess of acid was used. The following additional equations (analogous to those already given on page 134 of the article just mentioned) are necessary in order to reduce the result to the more generally useful equation:

$$\text{Zn} + 2(\text{HCl}.200\text{H}_2\text{O}) = \text{ZnCl}_2.400\text{H}_2\text{O} + \text{H}_2 + Q\ \text{kilojoules}.$$

In the first place the heat evolved by the dilution of all the hydrochloric acid is needed, in the next place the heat of dilution of all the residual solution, and finally the heat of mixture of dilute solutions of zinc chloride and hydrochloric acid. These are given in order below:

$$20.69(\text{HCl} + 20\text{H}_2\text{O}) + 3724\text{H}_2\text{O} = 20.69(\text{HCl} + 200\text{H}_2\text{O}) + y\ \text{kj}. \quad (2)$$

$$(\text{ZnCl}_2 + 18.69\ \text{HCl} + 414\text{H}_2\text{O}) + 3724\text{H}_2\text{O} = (\text{ZnCl}_2 + 18.69\text{HCl} + 4138\text{H}_2\text{O}) + z\ \text{kj}. \quad (3)$$

$$(\text{ZnCl}_2 + 400\text{H}_2\text{O}) + 18.691(\text{HCl} + 200\text{H}_2\text{O}) = (\text{ZnCl}_2 + 18.69\text{HCl} + 4138\text{H}_2\text{O}) + q\ \text{kj}. \quad (4)$$

From these equations, by simple elimination or cancellation, the desired result is easily found to be as follows:

$$\text{Zn} + 2(\text{HCl}.200\text{H}_2\text{O}) = \text{H}_2 + \text{ZnCl}_2.400\text{H}_2\text{O} + 126.8 - y + z - q\ \text{kj}.$$

Therefore the quantity sought, $Q = 126.8\text{kj}. + (z - y) - q$. It will be shown that the quantity q is zero in all the cases under consideration, hence it is clear that the ideal value for the heat of solution of the metal in dilute acid is to be obtained by adding to the heat of solution in concentrated acid the difference between the heat of dilution of the mixture remaining after the reaction and heat of dilution of all the acid originally taken. The fact that the quantity $(z - y)$ is a difference of similar quantities obtained in precisely the same way greatly increases the ease of determining it accurately, for any systematic errors in y would appear also in z, and hence be eliminated from the result $(z - y)$.

Similar sets of equations with the appropriate concentrations of acid must be used in the cases of aluminium, cadmium, and iron. In the case of magnesium, in which the proper concentration ($\text{HCl}.200\text{H}_2\text{O}$) of hydrochloric acid had been used in the first place, only one of these equations, that corresponding to (1) above, is necessary. Thus, in order to reduce the results given in the preceding paper to the same standard, eleven series of experiments on heat of dilution must be made, in order to determine the quantity y for two strengths of acid, the quantities z and q in four of the cases, and the quantity q in the fifth.

Before beginning the experimental work, two theoretical questions of great importance face the experimenter, namely, first, the question as to the temperature at which these dilutions should be conducted, and, secondly, the further question as to the heat capacity (whether that of the factors or that of the products) which should be used in the calculation of the several heats of dilution. These questions are connected with one another, and may be answered together.

At first it might be supposed that the heat of dilution of the hydrochloric acid should be measured at the initial temperature of the main reaction (namely, about 16°) because this is the only temperature in the process at which the acid solution exists unchanged. This interpretation is nevertheless illusory and erroneous. Although the main reaction of acid on metal takes place over the range from 16 to 20°, the result as calculated from the heat capacity of the factors corresponds to the heat given out by the reaction *conducted isothermally at the final temperature of 20°*.[1]

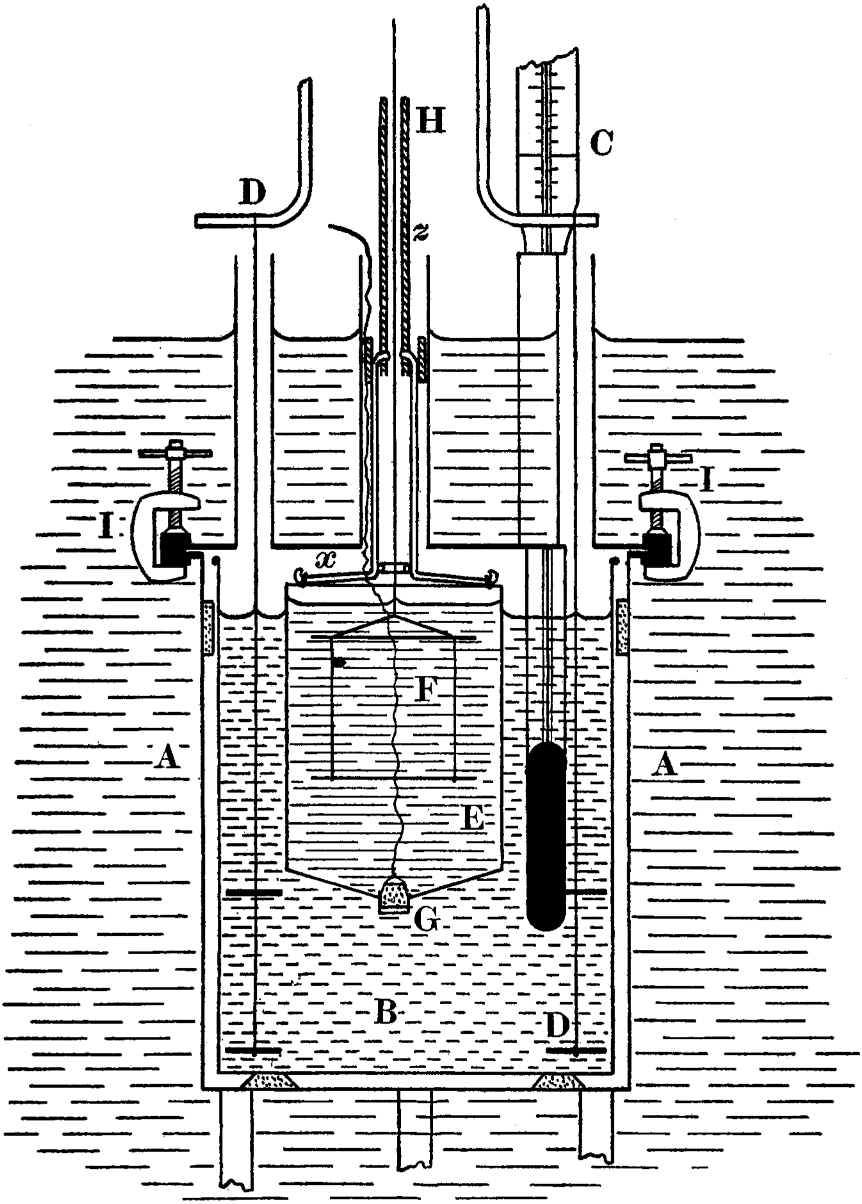
In thermochemical work precision in reasoning is only attained when all the data are reduced to an isothermal basis. Hence it is clear that all the dilutions must be conducted in such a way as to correspond to this same isothermal standard of 20°. This end may be effected in either of two ways: the dilution may be started at 20°, and the heat capacity of the product used in the calculation, or the dilution may be arranged so as to finish at 20° and the heat capacity of the *factors* used in the calculation. The latter method was used, because it was somewhat more convenient. Attention should perhaps be called to the fact that for the sake of ideal consistency, the specific heats used in these calculations should correspond to the small range of a few tenths of a degree just below 20°, and not to the whole range from 16 to 20°. This subtlety, however, may be safely overlooked in the present case, as the slight error which thereby arises in the individual data will appear in all, and will hence be cancelled in the final calculation of the quantity $(z - y)$. Moreover, because in the results to be tabulated, nine-tenths or more of the heat capacity was due to pure water (obviously, the chief factor in the dilution experiments) a large error in the specific heat of the concentrated solution produces very little effect on the result. Accordingly, the specific heats already given for the two acids, $HCl.8.808H_2O$ and $HCl\ 20.00\ H_2O$—namely, 0.7312 and 0.8486—were used in the calculation.

---

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

Calorimeter for Dilution Experiments.

For determining the heats of dilution of the acid liquids, that is to say, the parallel quantities y and z, special apparatus was needed. We employed for this purpose a device essentially similar to that used by Rich-



ards, Henderson, and Forbes in a previous investigation.[1] In this apparatus the concentrated solution was enclosed in a receptacle partly immersed beneath the water in the calorimeter; when both liquids had attained exactly the same temperature, the inner vessel was put into connection with the outer, and by suitable stirring the fluids were mixed.

The special form of apparatus used in this case was slightly different from that employed in the previous investigation. It is shown in the accompanying diagram. The inner vessel consisted of a platinum cylinder wholly open at the top, and having a small opening in the bottom. It was suspended on stout platinum wires, connected with thin hard-rubber rods above. The hole in the bottom was stopped by means of a small rubber stopper, the handle of which projected through the cover of the calorimeter. The inner vessel was filled with the solution to be diluted, and a small hand-driven propeller (made by sealing pieces of platinum foil to the sides of a thin-walled glass tube) served to stir it. The calculated amount of water was placed in the outer calorimeter, and the apparatus was adjusted to the position shown in the diagram. The thermometer was a new, very carefully calibrated instrument with degrees 10 centimeters long. When it had attained constancy after a prolonged stirring of both liquids, the plug was pulled out, and the inner platinum vessel lowered until it was entirely immersed in the water, the acid being free to escape both above and below. The liquid in the innner platinum vessel was then easily mixed with the water outside, because the outer stirrer, consisting of two rings of stout platinum foil with a vertical stroke, forced the liquid backwards and forwards through the inner cylinder after the fashion of a pump. The whole calorimeter vessel was enclosed in a larger copper vessel, nickel-plated inside and provided with tubes above for the stirrer, thermometer, and actuating mechanism. This "submarine" apparatus was surrounded by a concentric jacketing vessel, containing dilute alkali to which was added sulphuric acid at such a rate that the outer temperature exactly kept pace with the inner. The heat capacity of all the platinum parts, the rubber stopper, and the thermometer were equivalent to a sum total of 15.37 grams of water. The heat evolved by the stirring apparatus in the inner calorimeter was determined as a part of each experiment. The rate of the motor was such that it was usually sufficient to raise the temperature of the calorimeter at a rate of 0.004° in 10 minutes, the maximum time of the experiment. The correction is duly applied in each case for this extra heat.

There follow the experimental results for the heats of dilution of the two more concentrated solutions of hydrochloric acid. This table explains itself and presents no obscure features. Incidentally it may be remarked that the heat of dilution of $HCl.20H_2O$ at 16°, four degrees

---

[1] *Proc. Am. Acad.*, **41**, 11 (1905). *Z. physik. Chem.*, 52, 560 (1905).

lower than that mentioned in the table below, was also determined and found to be not far from seven per cent. less than the values given below. These results, however, do not concern the present investigation, and will be published in another connection.

Heat of Dilution of Hydrochloric Acid at 25°.

Expt. No.	Reaction measured.	Temp. of experiment.	Corrected rise of temperature.	Heat capacity in Cal./t° units.	Average energy change, Cal.	Energy change for 1 mol. HCl in large Calories.
1	130.0 grams HCl.20.H_2O + 1062.5 grams H_2O	19.88	0.152	1188.1	181.5	0.556
2		19.93	0.153			
3		19.93	0.153			
4		19.93	0.153			
5	60.0 grams HCl 8.8H_2O + 1059 grams H_2O	19.8	0.365	1118.3	408.2	1.330
6		19.8	0.366			
7		19.8	0.366			
8		19.8	0.366			

The numbers given in the last column of the foregoing table indicate that when to $HCl.20H_2O$ is added $180H_2O$, 0.556 Calories of heat are evolved at 20°, and that when $HCl.8.81H_2O$ is diluted with $191.2H_2O$, 1.330 Calories are evolved. For use in calculating the value y in several equations, these numbers must of course be multiplied by the number of moles of hydrochloric acid concerned in the actual reaction. For instance, in the case of zinc one gram atom of the metal was dissolved in a solution containing 20.69 moles of $HCl.20H_2O$. Therefore y in this case equals 0.556 × 20.69 or 11.5 Calories. Other factors are obviously necessary in the other cases; these factors will be named later.

The preliminary experiments with the solutions left in the calorimeter after the metals had been dissolved in the acid showed that considerable change in the heat of dilution is caused by the presence of the metal instead of hydrogen, which it had displaced. Thus the heat of dilution of the solution containing zinc was found to be over 0.08° more than the hydrochloric acid and the aluminium a few thousandths of a degree. On the other hand, the heat of dilution of the solution containing cadmium was less than that of the hydrochloric acid from which it was made by about 0.02° and the ferrous chloride solution remaining from the experiment with iron showed a very slight difference indeed, when compared to the pure acid. These results show that the heats of dilution may be a very serious factor in the result, and that they must therefore be determined with the greatest possible care. The next table records these very careful experiments, giving the heats of dilution of the mixed solutions remaining after the reaction, solutions which still contained a large excess of hydrochloric acid, but also a small amount of the dissolved chloride of the metal. These determinations were made in precisely the same way, as nearly as possible, as the experiments with pure hydrochloric acid. The same part of the thermometer was used, so that undetected errors in calibration, if present, would be automatically cancelled from the final result.

The dilution of the ferrous chloride solution presented some difficulty, owing to its tendency to oxidize. Obviously, results obtained with a solution which had oxidized either before or during the dilution experiment would be worthless. To prevent the solution from oxidizing before use, it was prepared in a flask connected with a hydrogen generator and fitted with a siphon and a delivery tube. In this way an atmosphere of hydrogen was maintained above the solution, and no oxidation could occur. The end of the siphon was kept under toluene, and the first portion discharged always rejected. During the experiment the surface of the liquids, both in the platinum container and in the calorimeter can, were covered with a layer of toluene, which sufficiently prevented access of air during the brief time of the experiment. The water used was, of course, boiled to free it from dissolved air. The toluene was first weighed into the inner platinum vessel and then the end of the siphon, which was drawn out to a long capillary, was inserted below the surface of the toluene and the ferrous solution allowed to run. When carried out in this fashion, the solution contained only the merest trace of ferric salt previous to the mixing, and after the mixing had been accomplished there was no appreciable increase, as estimated by colorimetric comparison, with sulphocyanate.

In order to calculate the heat of dilution the heat capacity of the two liquids being mixed must be known. One of these is pure water, the other a solution of hydrochloric acid containing a small amount of metal. From the results of Marignac it seemed probable that the substitution of the small amount of metal for some of the hydrogen in the acid would not have a very great effect upon the heat capacity of a given quantity of the acid. From his results it is apparent, for example, that the conversion of $2(HCl.25H_2O)$ into $SrCl_2.50H_2O$ causes a change in heat capacity of only about 1 per cent. Data in other cases are lacking, but this case may be taken as typical.[1] In order to make assurance doubly sure, however, the case of zinc (which gave the most divergent results) was tested with great care. 636 grams of $HCl.20H_2O$ were treated with about 5 grams of zinc. When the solution was complete, the specific heat of the resulting mixture was found by two very concordant results to be 0.8575. Hence the heat capacity of the total amount taken was $641 \times 0.8575 = 549$ "calorie units." The acid from which the solution was made had a heat capacity of 540. Thus there is a gain of heat capacity, owing to the substitution of zinc for hydrogen, of less than 2 per cent. Clearly this is a change too small to have any serious effect upon the re-

---

[1] *Ann. chim. phys.*, [5] **8**, 410 (1876).

sults of the heat of dilution; for the greater part of the heat capacity in dilution experiments is due to the water and not to the much smaller bulk of acid solution. An error of 2 per cent. in the heat capacity of the zinc solution would cause only 0.2 per cent. in the total heat capacity—a range of accuracy beyond one's ability to read the thermometers concerned in determining the heat of dilution. Because the most divergent case was that of zinc, it seems clear that no important error would be introduced by assuming that the heat capacity of the solution in all the other cases is equal to that of the hydrochloric acid from which the solutions were made. In yet more accurate work this point would demand consideration.

A table containing four series of experiments wth these residual liquids is given below:

HEAT OF DILUTION OF FINAL SOLUTIONS.

Expt. No.	Reaction measured.	Initial temperature of experiment.	Corrected rise of temperature.	Heat capacity in Cal./t° units.	Energy change, Calories	Energy change for 1 gram atom. of chlorine in large Calories.
11	125.0 grams of zinc soln. + 1013.7 grams of water	19.95	0.238°	1136	0.2715	0.868
12		19.94	0.238			
13		19.99	0.240			
14		19.94	0.239			
15		19.96	0.240			
16	125 grams aluminium soln. + 1020.9 grams water	19.94	0.156	1142	0.1784	0.567
17		19.92	0.156			
18		19.95	0.156			
19		19.94	0.156			
20		19.96	0.157			
21	60 grams cadmium soln. + 1043.4 grams water	19.90	0.346	1102	0.3824	1.262
22		11.94	0.348			
23		19.93	0.348			
24		19.93	0.347			
25		19.94	0.348			
26	60 grams ferrous soln. + 1049.7 grams water	19.94	0.368	1109	0.4081	1.339
27		19.93	0.369			
28		19.94	0.368			
29		19.94	0.367			
30		19.94	0.367			

The data given in the last column of this table are used for the calculation of the quantity *z*, by multiplication with the appropriate factor. In the case of zinc, this factor is, as before, 20.69, because 20.69 molecules of hydrochloric acid were present for each atom of zinc. The other factors are given below in the next table.

The marked differences between the heats of dilution of the solutions containing small amounts of zinc and aluminium, but otherwise alike, is very interesting. The correspondence with the preliminary results is very close.

It is not necessary to give the full details of the careful experiments indicating the complete absence of heat of mixture of $(^1/_n MCl_n)\ 200H_2O$ with an excess of $HCl.200H_2O$. Ten experiments of this kind were made, two with each of the chlorides of zinc, aluminium, magnesium, cadmium, and iron in place of MCl_n. Exact weighing was not necessary in these cases because a slight excess of one or the other reagent would have a vanishingly small effect, since the total change to be measured was found to be imperceptible. In no case was a perceptible evolution of heat observed in these reactions. Hence the quantity q in the previous equations became 0 in each case, as has been already stated.

Calculation of Final Results.

The various data concerning dilution may now be applied to the heats of solution of the metals in concentrated acids, thus computing the theoretical value of the heat which the reactions would evolve in each case, provided that the metal were dissolved in just enough $HCl + 200H_2O$ to effect its complete solution, giving a product free from excess of acid. In order to accomplish this, there must be in each case subtracted from the value of the heat of solution actually observed for a gram atom of metal, the heat of dilution of the hydrochloric acid employed under the experimental conditions to act upon a gram atom of metal; and there must be added to the result the heat of dilution of the corresponding quantity of residual solution. The following table indicates the number of moles of acid corresponding to a gram atom of metal, the data being taken from the record of the experiments already given in the previous paper:

Molecular Proportions of Acid and Metal.

	Weight of metal.	Atomic weight.	Fraction of gram atom present.	Gram mols. of acid present.	Gram mols. of acid for each gram atom of metal.
Zinc	7.496	65.37	0.11467	2.372	20.69
Aluminium	0.747	27.1	0.02756	2.372	86.06
Magnesium	0.849	24.32	0.03492	...	...
Cadmium	14.983	112.32	0.13328	5.038	37.80
Iron	9.000	55.85	0.16114	5.037	31.26

The values given in the final column of this table are the factors needed in order to calculate the values of y and z from the values given in the last columns of the two preceding tables respectively.

The values for y and z calculated in this way from these data for each of the four metals, zinc, aluminium, iron, and cadmium, are given in the following table: The table contains the values for x, the heat of solution of the metal in the excess of concentrated acid (repeated from the previous paper), and also the final result sought, $x + (z - v)$:

Metal concerned.	x in Calories.	y in Calories.	z in Calories.	$x+(z-y)$ in Calories.	Thomsen's values.
Zinc	30.18	11.50	17.94	36.6	34.2
Aluminium	126.0	47.81	48.8	127.0	115.0
Magnesium	110.15	0	0	110.15	108.7
Cadmium	19.77	50.27	47.70	17.2	17.6
Iron	20.55	41.57	41.85	20.8	21.3

Thus the new values for the heats of reaction sought are as follows:

$Zn + 2HCl\ aq = ZnCl_2\ aq + H_2 + 36.6$ Cal. or 153.1 kilojoules.

$Al + 3HCl\ aq = AlCl_3\ aq + 3/2H_2 + 127.0$ Cal. or 531 kilojoules.

$Mg + 2HCl\ aq = MgCl_2\ aq + H_2 + 110.2$ Cal. or 460.6 kilojoules.

$Cd + 2HCl\ aq = CdCl_2\ aq + H_2 + 17.2$ Cal. or 71.9 kilojoules.

$Fe + 2HCl\ aq = FeCl_2\ aq + H_2 + 20.8$ Cal. or 87.0 kilojoules.

The comparison of the new results with Thomsen's values given in the last column shows that the new results differ in some cases considerably from the old value. These differences are to be explained partly by the defect in Rumford's method of correcting for cooling, as used by Thomsen, and partly by his having omitted to add to his results the excess of the heat of dilution of the product over that of the pure acid solution.

It is apparent that the present results are not all equally accurate. In the case of magnesium the result is obtained directly without the necessity of applying any correction for heat of dilution. It is therefore decidedly more certain than the others. In the case of zinc the individual values of the quantities x and y are not large, and supposing these values to be known within one per cent., the error of the final result probably is not more than 0.15 Calorie, or half of 1 per cent. In the case of aluminium the values y and z are larger in actual magnitude, but not larger in proportion to x, therefore the probable percentage error is about the same. In the case of cadmium and iron, the percentage of accuracy of the determination of y and z is greater because the change of temperature involved is greater, but the very large magnitude of each of these quantities (distinctly larger than that of the main reaction) more than neutralizes this advantage.

One favorable circumstance already alluded to mitigates considerably the damaging effect of these difficulties, namely, the fact that y and z are always opposite in sign and nearly equal in magnitude. Because they were observed in precisely the same way under almost similar conditions, it is reasonable to suppose that the same error, if any, applies to both, and that therefore the error would be eliminated.

In order to obtain better results, it would be necessary either to dissolve the metal in a much smaller quantity of less concentrated acid, so that the values y and z should be smaller, or else to observe with greater accuracy than was possible with any means of thermometric measurement at our disposal the heats of dilution of the several solutions. The purity of the metals used preventing the employment of a less concentrated acid because of their slow rate of solution, the latter alternative is perhaps the easier of the two. It is hoped in the near future that the experience gained in this research may be applied in a more complete manner. In the meantime the results here given must be looked upon as merely preliminary. At least it is hoped that the present papers have succeeded in putting the subject of the heats of solution of metals upon a sound scientific basis, to which the future can add nothing more than perfection of detail.

In conclusion, it is a pleasure to express our indebtedness to the generosity of the Carnegie Institution of Washington for pecuniary assistance.

Summary.

There follows in a few words a statement of the outcome of this paper:

1. The heats of dilution of the acids $HCl.20H_2O$ and $HCl.8.808$ to $HCl.200H_2O$ were determined. The results are 0.556 and 1.330 Calories (2.32 and 5.56 kilojoules) respectively.

2. The heats of dilution of the several products obtained by dissolving four metals in excess of concentrated acid were determined. The substitution of salt for acid was found, especially in the cases of zinc and cadmium, to affect seriously the heat of dilution.

3. From these data the heats of solution of a gram atom of the several metals in exactly the theoretical quantity of $HCl.200H_2O$ have been calculated as follows:

THE HEAT OF REACTION OF METAL ON $HCl.200H_2O$ CALCULATED FOR 1 GRAM ATOM OF METAL.

Metal.	Heat of reaction in 18° Calories.	Heat of reaction in Kilojoules.
Zinc	36.6	153.1
Aluminium	127.0	531.0
Magnesium	110.2	460.6
Cadmium	17.2	71.9
Iron	20.8	87.0

[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE INCONSTANCY OF THE SOLUBILITY PRODUCT.[1]

BY ARTHUR E. HILL.

Received July 11, 1910.

The various assumptions made by Nernst[2] and A. A. Noyes[3] in their earlier investigations on the solubility of electrolytes have been subjected

---

[1] Presented before the New York Section of the American Chemical Society, June 10, 1910.

[2] *Z. physik. Chem.*, **4**, 372 (1889).

[3] *Ibid.*, **6**, 241 and subsequent papers.