In particular, a demonstration is given of the at least approximate independence of the ordinary separation coefficient, for any element, of anything but the total molecular weight, even if the molecule contains other isotopic elements. Examples are also given in Table I of the extreme accuracy of the density comparisons which can be made with the pycnometer described in the previous paper.

It may be well to correct here certain conclusions given in the previous paper (pp. 40–41) in regard to the rate of separation of isotopes by gaseous diffusion, i. e., diffusion of an isotopic gas through a thin layer of another gas enclosed in the pores of a membrane. Briefly, this method is now found to be always *less* favorable than molecular diffusion, instead of *more* favorable, as previously concluded. This is due to the effect of the increased mean free path of the heavier molecules which results from persistence of velocity. This factor was expressly neglected before. Further, it now appears that mass motion, either positive or negative, should have practically no effect on the rate of separation, except indirectly as it may affect back pressure and so efficiency. A fuller discussion of this subject will be given later. Experimental work is now being carried on with mercury.

Acknowledgment should have been expressed in the previous paper of indebtedness to the C. M. Warren Fund of the American Academy of Arts and Sciences for a grant of five hundred dollars made to Professor William D. Harkins. A part of this grant was used in the purchase of an extremely accurate balance which was available for use in the previous investigation on the separation of the isotopes of mercury by the evaporation method, as well as in the present work.

CHICAGO, ILLINOIS

THE HEAT OF SOLUTION OF ZINC IN HYDROCHLORIC ACID

BY THEODORE W. RICHARDS AND THORBERGUR THORVALDSON

The heats of solution of metals in acids—data which are the basis of the computation of the heats of formation of all compounds of metals—are worthy of especial attention. The incompleteness of Thomsen's method of correcting his results for the heat of dilution of the solutions employed[1] and the merely approximate character of early work renders revision desirable.

Revision was, indeed, begun over a decade ago. Values for the heat of solution of zinc, aluminum, magnesium, cadmium and iron in hydrochloric acid were found which in some cases differed markedly from Thomsen's

---

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

values.[2] This research was, however, preliminary in character. As was duly indicated, the needful corrections for the heats of dilution of the solutions were sometimes so large as to cause uncertainty. The present communication presents a repetition of the experiments with zinc under better conditions. The new results substantiate the old ones within a reasonable limit of error but are, nevertheless, so much more satisfactory that it is worth while to recount them in detail. The experimental work was finished in 1914, but as usual the publication has been delayed.

Apparatus.—Since the chief difficulty in the preliminary work ᴵlay in the large volume of acid employed for dissolving the zinc, a new arrangement was devised which permitted the use of a much smaller amount of acid, thus greatly diminishing the error which might arise from the corrections due to the heat of dilution. In order that a relatively large amount of zinc should be dissolved in this small amount of acid, without causing undue rise of temperature with its attendant complications, a large heat capacity was provided by immersing the reaction vessel in a large calorimeter filled with water. The whole was surrounded by an environment which could be changed in temperature so as to assure adiabatic conditions. The outer parts of the apparatus, including the 1.4-liter platinum calorimeter can, were identical with those used in the preliminary work, but the reaction vessel should be described in detail.
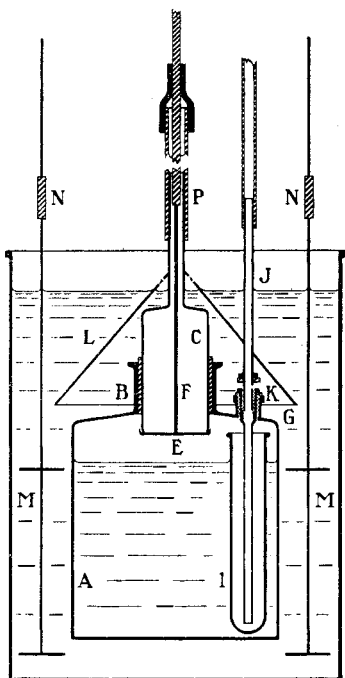
The Inner Calorimetric Vessel and Appurtenances.

This vessel was enclosed (with surrounding air space) in a water-tight envelope with tubes above. The envelope was immersed in a large bath, which was always kept at the same temperature as the inner vessel.

This reaction vessel consisted of a bottle (200 cc. in volume) of pure gold (A in the diagram) with two outlets above (B, G). The gold stopper (C) in the wider central outlet was made tight by a rubber band and contained, below, a movable inverted cap (E) for holding the zinc, which was thus kept within the bell-shaped stopper until the moment of beginning the experiment. At this moment the cap was lowered into the acid in the gold bottle and used as a stirrer.

In order to eliminate spray, the evolved hydrogen was caused to pass out of the bottle by a circuitous route. downward into a gold test-tube (I) contained within the bottle and then upward through a fine platinum side

[2] Richards, Rowe and Burgess, THIS JOURNAL, 32, 1176 (1910).

tube reaching almost to the bottom of the test-tube within the bottle. This test-tube also served to prevent reflux water from mixing with the contents of the bottle. The hydrogen afterwards emerged through water in the outer can, giving up its surplus heat and becoming saturated with water vapor. The screw stopcock (K) could, by turning, be closed at the start and conclusion of the experiment, being operated by a hard rubber tube attached to the platinum tube (J). The rubber tube (which projected from the top of the calorimeter jacket) could be closed above. An unsymmetrical cone of platinum foil (L), the apex of which reached a little above the surface of the liquid in the calorimeter, prevented the bubbles from spattering liquid upon the cover of the calorimeter. The stirring of the water in the main calorimeter was effected by a vertically reciprocating 2-stage stirrer of the conventional type, made of pure silver. This also, like the outside connection of the gold stopper and the platinum side tube, was thermally insulated by means of hard rubber. The assemblage is suitable, with minor modifications, for determining a great variety of thermochemical values, especially such as involve the absence of water in the reacting vessel.

The apparatus used for determining specific heats and heats of dilution has already been described in full in the earlier papers of this series.

All parts of each of these assemblages were individually weighed for the computation of the heat capacities.

The Beckmann thermometer employed had been carefully standardized in a variety of ways. The standardization finally accepted was that kindly carried out by O. C. Bridgeman and confirmed calorimetrically by S. Tamaru.[3] A thermometer of similar construction was used in the outside bath and one reading to 0.1° for the determination of the room temperature.

All temperature readings and all corrections were made to 0.0001°, and the result was then rounded off to the nearest thousandth. Hence, as far as possible, no single value should be more than 0.0005° in error.

The *averages* of many readings should be still better. Of course this limit of error applies only to the readings; it does not apply to any possible unknown constant error.

Materials.—Two samples of zinc were used in this work. One was the "reagent zinc," identical with that used earlier,[1] and found to give results identical with those from the most carefully purified electrolytic zinc. This specimen had been carefully analyzed and found to contain no amounts of impurity which could affect the present results. The second sample, B, was guaranteed "the purest zinc for analysis" and was found to be even purer than Sample A. The granules of metal were hammered into thin sheets, using a brightly polished hammer and anvil of the best tool steel. The trace of iron thus introduced could not have produced any essential effect on the thermochemical result. The thin sheets of zinc were kept in the desiccator over caustic alkali until needed. Hydrochloric acid was prepared from the purest acid of commerce by dilution with an equal amount of distilled water and distillation in a quartz container. The second third of the distillate was collected and made up exactly to the required strength, $HCl.20H_2O$. The final determination of the exact concentration was made by duplicate gravimetric silver chloride analyses. All quantities of materials were

[3] Richards and Tamaru, THIS JOURNAL, **42**, 1376 (1920).

measured with weights compared with the international standard, and were reduced to that standard, as well as corrected to vacuum.

The knowledge of several specific heats was needed for the calculation of the results. The specific heat of HCl.20H$_2$O had previously been found to be 0.849.[4] By means of the apparatus employed in determining this datum, it was found that the specific heat of the solution remaining after the reaction of zinc on hydrochloric acid was 1.62% greater than that of the acid given above; this specific heat was therefore taken as 0.863. The specific heats of zinc, platinum, gold and silver were taken, respectively, as 0.092, 0.0324, 0.0312, and 0.055, while that of rubber was taken as 0.48. The specific heat of water was taken as 1.000 at 18° because the heat capacities were determined over the range 16° to 20°. Afterwards, all the results were reduced to 20°, using the 20° calorie.

Details of Experimentation

The requisite amount of water was weighed in the platinum calorimeter vessel, and of HCl.20H$_2$O in the gold bottle, the gold test-tube and the connecting platinum tubes having been placed in position. The gold stopper (filled with a suitable weighed quantity of zinc, and with its trap-door below closed) was then fitted very tightly into the gold bottle, the screw valve (K) was closed, and the whole assemblage lowered into the calorimeter to a suitable depth, as indicated in the diagram. The bottle was held in position by means of the stout hard rubber extension (P) attached to the stopper. When the system had adjusted itself to a constant thermal condition, as indicated by the very slight regular change in thermometric reading produced by stirring, the trap-door cap (E) at the bottom of the stopper was pushed down (without breaking the air-tight joint above) thus immersing the zinc in the acid. By turning the side tube (J) after closing the valve at its top, the outlet at (K) was opened, and the hydrogen evolved was forced through the water. The bubbles, striking against the sheath afforded by the platinum cone, rolled up the inside of its surface and broke inside the cone. The gas escaping through small perforations in the platinum foil caused but very little spray. As long as the tubes (P) and (J) were closed at the top there was an excess of pressure of hydrogen within the gold bottle. Even if this, through leakage, was momentarily relieved, the gold test-tube acted as a trap to prevent water from mixing with the acid, thus yielding accidental heat of dilution.

When the solution of zinc was almost complete, as shown by the greatly diminished rate of temperature-rise, the outlet (K) was closed, and the valve at the top of P opened, the last trace of hydrogen being allowed to escape under atmospheric pressure into the air. The liquid within the gold bottle was then stirred by means of the lowered trap-door, until uniform

[4] Richards and Rowe, THIS JOURNAL, **42**, 1628 (1920).

temperature was obtained throughout. On dismantling the apparatus the water in the calorimeter was in each case tested to discover if any acid had found its way out of the gold bottle, but none was ever found. The gold test-tube never contained more than a few drops of liquid except in early cases of faulty manipulation. The whole with its contents was weighed after each determination in order to make sure that no water had entered from outside.

The Heat of Solution of Zinc in Concentrated Hydrochloric Acid

Two preliminary series, of a few experiments each, were made by dissolving small amounts of zinc in acid in the apparatus thus assembled. They gave, within a reasonable limit of error, essentially the same result as the final series but, having less weight and adding little to the outcome, they were hardly worth publication. They served to perfect the details of experimentation and also, by their agreement, showed that no gross mistake had been made in any case.

The final series was much more trustworthy than the earlier ones and covered a greater range of temperature. Every experiment of this final series is included in the table below. For each, 9.000 g. of zinc was taken, and 170.00 g. of $HCl.20H_2O$ was placed in the inner flask, quantities having the ratio $Zn: 3.1116 \ HCl.20H_2O$. This flask was surrounded by 934.3 g. of water. The sum of these three heat capacities is 1079.4. From this must be subtracted 0.5, half the heat capacity of the moist hydrogen evolved, which should have been heated instead of being allowed to escape,[5] if the method of calculating the thermal result is rigorously applied. Finally, of course, the heat capacity 20.50 of the apparatus must be added. This latter quantity was made up as follows: platinum parts, 6.48; gold parts, 5.92; silver stirrer, 3.86; rubber, 0.81; thermometer, 3.42. Thus the total heat capacity of the system was taken as 1099.5 cal.$(18°)/t$.

The experiment, which lasted about half an hour, was conducted by the usual adiabatic method. The rise of temperature was so slow that the experimenter could keep the temperature of the environment very close to that of the inner vessel; it was always kept 0.01° or 0.02° above that of the calorimeter proper.[6] The outlets admitting the stirrer-shafts were duly plugged with cotton wool to prevent evaporation. If any cooling from this source took place, it must have been accounted for in the stirring correction, which was carefully determined before and after the experiment. Because of the length of time and of the necessity of preventing thermal stratification in the calorimeter, this correction was large, but in the series

[5] The first bubble was not heated at all; the last was evolved at the final temperature. Hence the correction is half the total heat capacity of the moist hydrogen under constant pressure.

[6] Ref. 1, p. 449.

given, it was possibly known within $0.001°$ and almost certainly within $0.002°$. Therefore it did not introduce a serious disturbing element. The designations t_1 and t_2 in the table below are respectively the initial and final thermometer readings corrected to the standard of the platinum resistance thermometer. The correction (never more than $0.002°$) for the temperature of the exposed stem of the thermometer is entered with the stirring correction. The eight determinations of the final series showed a maximum range of $0.003°$ on each side of the mean.

TABLE I

SOLUTION OF 9.000 G. OF ZINC IN EXCESS OF HCl.20H$_2$O (170.00 G.)

Expt.	Sample zinc	t_1 °C.	°C.	t_2-t_1 °C.	Correction for stirring and stem °C.	Corrected rise of temperature °C.
1	B	16.034	20.161	4.127	-0.022	4.105
2	B	16.943	20.073	4.130	-0.026	4.104
3	B	16.946	20.076	4.130	-0.023	4.107
4	A	16.957	20.082	4.125	-0.018	4.107
5	A	16.989	20.108	4.119	-0.018	4.101
6	B	16.967	20.084	4.117	-0.012	4.105
7	A	16.943	20.069	4.126	-0.024	4.102
8	B	16.936	20.050	4.114	-0.012	4.102
						4.104

The heat capacity of 1099.5 Cal.$(18°)/t°$ was evidently heated through $4.104°$, and the heat thus measured was 4512.4 Cal.(18°). In terms of Cal.(20°) this is 4514.4.

For a gram atom the heat of this reaction of zinc on HCl.20H$_2$O (56% in excess) was 32.789 Cal.(20°), or 137.06 Kj., if one Cal.(20°) $= 4.180$ Kj. Since the heat capacities of the factors were used, the result is the isothermal heat of reaction at $20.09°$, the average final temperature.

The temperature coefficient of this reaction is easily computed, since the Kirchhoff rule applies to heats of reaction as well as to total energy changes, if consistently used. The increase of the total heat capacity during the reaction (conducted isothermally) is found from increase of heat capacity of the contents of the inner flask, as follows.

Heat capacity of acid and zinc $= 170.00 \times 0.849 + 0.81 = 145.14$
Heat capacity of zinc sol. and (moist gas) $_p = 178.68 \times 0.863 + 1.10 = 155.30$
Gain $= \overline{10.16}$

The very striking increase, 10.16, or about 7%, represents the gain of heat capacity which occurred when 9.000 g. of zinc (or 1/7.2633 gram atom) was dissolved. For a gram atom of zinc the corresponding amount is 74 cal. t which (with negative sign) equals the temperature coefficient of the reaction, Thus at $20°$ the heat evolved under the above conditions would be 32.795 Cal.(20°).

Heats of Dilution of Factors and Products

Since the heat of the reaction $Zn + 2HCl.200H_2O = ZnCl_2.400H_2O + H_2$ was desired, it was necessary to determine the heats of dilution of the more concentrated acid used for dissolving the zinc as well as the heat of dilution of the product.[7] These heats of dilution were determined in apparatus which has already been described in full.[8] The combination designated Ab was used, and as arranged in these experiments, the apparatus had a heat capacity of 15.06 cal./t units. In each experiment 125.00 g. of solution was employed. The results for the respective rises of temperature follow.

TABLE II

DILUTION OF HYDROCHLORIC ACID

No.	t_1	t_2	Stirring correction	$t_2 - t_1$ corrected
	° C.	° C.	° C.	° C.
1	19.896	20.054	−0.006	0.152
2	19.898	20.057	−0.007	0.152
3	19.809	20.963	−0.001	0.153
4	19.736	20.890	−0.001	0.153
5	19.750	20.903	−0.001	0.152
6	19.729	20.882	−0.001	0.152
7	19.726	20.879	−0.001	0.152
				0.1523

DILUTION OF IMMEDIATE PRODUCT OF ZINC REACTION

8	19.588	20.034	−0.003	0.443
9	19.588	20.034	−0.003	0.443
10	19.614	20.058	−0.001	0.443
11	19.609	20.054	−0.002	0.443
12	19.592	20.036	−0.001	0.443
				0.443

The result with hydrochloric acid is essentially identical with that found in a previous research.[9] The calculation of the change in heat-content produced by the respective dilutions leads then to the following quantities.

For pure acid solution $(15.06 + 125.0 \times 0.849 + 1021.6) 0.1523 = 174.04$ cal.

For acid zinc solution $(15.06 + 125.0 \times 0.863 + 970.2) 0.443 = 484.2$ cal.

These values must be multiplied by 170/125 and 178.68/125, respectively,[10] to find the heats of dilution of the amounts actually concerned in each experiment involving the solution of zinc in acid; 236.7 and 692.1, respectively, are the results. To correspond with a gram atom of zinc,

[7] Ref. 1, p. 433.
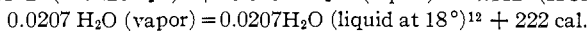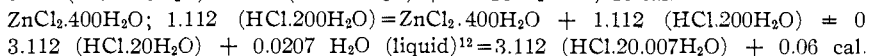
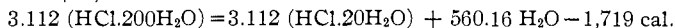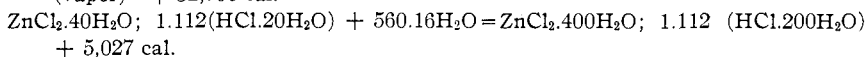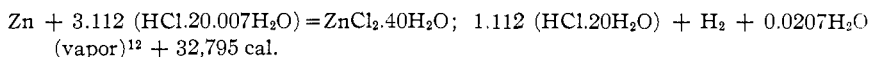[8] Ref. 2, p. 1178.   Ref. 4, pp. 1622, 1625.

[9] Ref. 4, p. 1631.

[10] The weight of the product is of course made up of the sum of the weights of acid and zinc less the weight of moist hydrogen evolved $(170.00 + 9.00 - 0.32 = 178.68)$. The small amount (0.051) of water lost by evaporation affects the heat of dilution but little.

these values should each be multiplied by 7.2633, yielding 1719 cal. and 5027 cal., respectively.   Mixing HCl. $200H_2O$ and $ZnCl_2.400H_2O$ was found in two trials to evolve no appreciable amount of heat.

One further calculation is necessary, namely, of the heat of evaporation of the water carried away by the hydrogen.   The average vapor pressure of pure water between 16° and 20° is 15.53 mm.;   therefore (the average atmospheric pressure during the experiments having been 758 mm.) the average volume of the moist hydrogen in each experiment must have been $\dfrac{22.4 \times 758 \times 291.1}{742.5 \times 273.1 \times 7.2633} = 3.365$ liters.   Since at that average temperature each liter of water vapor weighs 15.29 mg. and the latent heat of evaporation is 593, the evaporation must have needed 30.5 cal.   For a gram atom of zinc the quantity of heat absorbed would be 222 cal.[11]

All the data are now at hand for the calculation of the heat of the reaction $Zn + 2(HCl.200H_2O)$ at 20°.   This calculation may be expressed as follows, the semicolon indicating a mixture of solutions, and all the quantities being expressed on a consistent molal basis:

$Zn + 3.112$ $(HCl.20.007H_2O) = ZnCl_2.40H_2O;$ 1.112 $(HCl.20H_2O) + H_2 + 0.0207H_2O$
   (vapor)[12] $+ 32,795$ cal.
$ZnCl_2.40H_2O;$ $1.112(HCl.20H_2O) + 560.16H_2O = ZnCl_2.400H_2O;$ 1.112 $(HCl.200H_2O)$
   $+ 5,027$ cal.
3.112 $(HCl.200H_2O) = 3.112$ $(HCl.20H_2O) + 560.16$ $H_2O - 1,719$ cal.
$ZnCl_2.400H_2O;$ 1.112 $(HCl.200H_2O) = ZnCl_2.400H_2O$ $+$ 1.112 $(HCl.200H_2O)$ $\doteq 0$
3.112 $(HCl.20H_2O)$ $+$ 0.0207 H_2O (liquid)[12] $= 3.112$ $(HCl.20.007H_2O)$ $+$ 0.06 cal.
   0.0207 H_2O (vapor) $= 0.0207H_2O$ (liquid at 18°)[12] $+ 222$ cal.
Therefore $Zn + 2$ $HCl.200$ $H_2O = ZnCl_2.400$ $H_2O + (H_2)$ $_p + 36,325$ cal. (20°) or $+ 151.8$
   Kj. (1 Cal. $= 4.18$ Kj. at 20°)

Instead of this value, 36.32 Cal., Thomsen found 34.2 (in error largely because his correction for dilution was erroneous in principle) and Richards, Rowe and Burgess in their preliminary study found 36.6.   The new value is doubtless more accurate than the older ones.

The value 36.32 Cal. corresponds to the isothermal reaction at 20° in which the hydrogen evolved is dry, a condition not attained in practice. To find the actual result of the isothermal reaction at 20° involving moist hydrogen, the latent heat of evaporation of about 0.42 g. of water, that is to say, about 0.25 Cal.,[13] should be subtracted, leaving 36.07 Cal. or 150.8 Kj. as the final result.

[11] For a fuller discussion of this subject see Ref. 1, pp. 450–452.

[12] This quantity of water is too small to affect essentially the heats of dilution. It is important only because of its heat of vaporization, but is introduced in the first and fifth equations for the sake of completeness of thermochemical statement.

[13] The value 0.222 Cal. given previously corresponds to the actual adiabatic reaction between 16° and 20°.   The value 0.25 corresponds to the evaporation from the very dilute acid or zinc chloride solution at 20°.

The temperature coefficient of this reaction cannot be computed accurately with the data on hand, since the heat of dilution of the product of the first of these processes has been determined accurately only at a single temperature. Probably, however, it is negative, and may amount to at least 25 cal. per degree, since the product contains one ion less than the factors, and at this concentration is probably less ionized than the factors;[14] de Marignac's experience supports this conclusion.[15] He found that $ZnCl_2$. $200H_2O$ has 39 less heat capacity than 2 HCl. $100H_2O$, and that the difference with double these concentrations was -68. His specific heat determinations were usually remarkably accurate considering the simple means employed. Our own experience with a still more concentrated acid solution ($20H_2O$) which showed a difference of -73 cal. per degree is confirmatory. The difference in heat capacity between metallic zinc and hydrogen is negligible in this connection. Assuming that at infinite dilution the loss of one gram-ion would make a difference of $+25$[16] and plotting the smooth, almost linear curve between this value and the values for the two concentrations studied by de Marignac, we arrive at the value of about -30 cal. per degree as the temperature coefficient of the reaction of zinc on 2 (HCl. $200H_2O$). Until more direct knowledge is available, this value may be assumed as the most reasonable one.

The value 36.32 Cal. is the heat of reaction corrected for the heat of vaporization of water carried away by the hydrogen, but uncorrected for outside work done against atmospheric pressure by the hydrogen. This latter amounts to $\left(\dfrac{291.1 \times 22.4}{273.1}\right) 0.0242 = 0.58$ Cal. The work done by the small amount of aqueous vapor (which augmented the volume of hydrogen by about 0.4 liter) has already been accounted for in the heat of its evaporation. Hence the energy change (U) of the reaction in question is found to be 36.90 Cal. or 154.2 Kj.

With the help of S. Tamaru, cadmium has been studied in the same way. The result is communicated in the following paper.

·

Summary

1. A new apparatus is described, suitable for dissolving substances

---

[14] Richards and Rowe, THIS JOURNAL, **43**, 793 (1921).

[15] C. de Marignac, "Oevr. Compl." Geneva, II, 624.

[16] Ref. 14, pp. 793, 795. This is the most probable value for the change of heat capacity caused by the simple subtraction of a single gram-ion. Whether this same change occurs when a bivalent ion takes the place of two univalent ones is not certain, since adequate data are lacking.

in a comparatively small excess of liquid and providing a conveniently large heat capacity for the reception of the heat.

2.   With this apparatus the heat of the reaction $Zn + 2HCl.200H_2O = ZnCl_2.400H_2O + H_2$ was found to be 36.32 Cal. (or 151.8 Kj.) if the hydrogen is dry, and 36.07 Cal. (or 150.8 Kj.) if the hydrogen is moist, at 20°.

3.   The total energy change (U) of this reaction is therefore 36.90 Cal. (or 154.2 Kj.) at 20°.

4.   The heats of dilution of factors and products needed for the attainment of these results were found experimentally.

5.   Attention was paid to numerous minor details which have usually been overlooked.

6.   The temperature coefficient of the heat of solution of zinc in conc. hydrochloric acid is shown to be negative and of considerable magnitude; even with dil. acid it probably amounts to −30 cal. per degree.

CAMBRIDGE 38, MASSACHUSETTS

THE HEAT OF SOLUTION OF CADMIUM IN HYDROCHLORIC ACID

By THEODORE W. RICHARDS AND SETSURO TAMARU

The importance of a revision of fundamental thermochemical data with modern accuracy has been repeatedly emphasized.   Among the metals treated in an earlier preliminary communication, cadmium was the least satisfactorily studied, as was pointed out at the time.[1]   Considerable improvement in method, already applied in the case of zinc,[2] was applicable likewise to the case of cadmium, with minor changes.   The present paper communicates the result of work carried out during the winter of 1914–1915.   The work on zinc having been described in detail, a briefer account now suffices.

In order to gain further experience with the apparatus and to confirm its trustworthiness, a few trials were first made with zinc, repeating the work described in the previous paper just mentioned, under somewhat different conditions.   The last two (naturally the most successful) of these experiments each involved the solution of 7.001 g. of zinc in 170.04 g. of $HCl.19.76H_2O$ (containing a drop of chloroplatinic acid), surrounded by 943.6 g. of water.   The increments of temperature of these two experiments were respectively 3.116° and 3.113°, with all thermometric

---

[1] Richards and Burgess, THIS JOURNAL, **32,** 459 (1910).   Richards, Rowe and Burgess, *ibid.,* p. 1185.

[2] Richards and Thorvaldson, *ibid.,* **44,** 1051 (1922).