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

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

# THE HEAT OF SOLUTION OF CADMIUM IN HYDROCHLORIC ACID

BY THEODORE W. RICHARDS AND SETSURO TAMARU

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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

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

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

corrections applied, the final temperatures being 20.30° and 20.43° respectively. The total heat capacity was 1103.4; and 3.1145° × 1103.4 = 3436.5. Corrected for the heat of depositing 7.5 mg. of platinum (as will be explained shortly) the result becomes 3434. cal., which corresponds to 0.1071 gram atom of zinc and 0.4332 mol. of $HCl.19.75H_2O$; hence for 1.0000 gram atom of zinc the evolution of heat under these circumstances would be 32.064 Cal. This output of heat corresponds to the isothermal reaction at 20.36°. According to the previous investigation, it would be 26 cal. more at 20°, making 32.090 Cal. The heat of dilution of the corresponding 4.045 mol. of hydrochloric acid is easily found from earlier work;[3] and that of the resulting solution of zinc was duly determined, 109.34 g. of this solution (sp. heat = 0.864) causing a rise of 0.422° when diluted with 869.0 g. of water in the usual apparatus. The total dilution-effects were thus shown to be respectively 2.237 and 6.238 Cal. for quantities corresponding to a gram atom of zinc, and the heat removed by evaporation of the water at 18.8° with the hydrogen must have been 234 cal. Therefore the total output of heat as found in the reaction $Zn + 2HCl.200H_2O = ZnCl_2.400H_2O + (H_2)_p$ at 20° would be $32.090 + 6.238 - 2.237 + 0.234 = 36.325$ Cal. If Thorvaldson's value for the heat of dilution of hydrochloric acid had been used, the result would have become 36.335. These are in as close agreement as could be expected with the more thorough work of one of us with Thorvaldson, which gave the value 36.325. In the present repetition less zinc was used, involving a change in every one of the corrections.

Such an agreement justified the application of the method to other substances; and no modifications in the apparatus seemed to be necessary. The only important changes were the use of more concentrated hydrochloric acid and the addition of a larger amount of chloroplatinic acid, both changes being necessitated by the lower solution tension of cadmium. The thermometers and their standardization were identical, and precisely the same apparatus of gold and platinum was used in the adiabatic calorimeter, in essentially the same way. The only change in technique was a decrease in the rate of stirring, which was permissible because the reaction with cadmium was somewhat slower and the temperature change was much less. The stirring rate (about 50 strokes per minute) caused a rise of only 0.001° in 30 minutes when the environment was 0.01° to 0.02° warmer than the calorimeter. Perhaps part of the heat from stirring was balanced by a very small cooling effect from evaporation. In any case, a net correction of 0.002° per hour was justified by the performance of the apparatus under the conditions employed.

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[3] Richards and Rowe, This Journal, **42,** 1632 (1920); **43,** 786 (1921). The heat of dilution of $HCl. 19.75 H_2O$ to $HCl.200H_2O$ would be 553, *i. e.*, 4 cal. more than the heat of dilution of $HCl.20 H_2O$ to the same limit.

Once more the effect of varying the thickness of the air space, which serves as thermal insulator around the calorimeter, was tested with this apparatus. A thickness of 7 mm. was found to involve a transfer of 0.008 cal. per minute per sq. cm. per 1° thermal head. Enlargement of the space to 18 mm. showed no advantage; restriction to 4.5 mm. raised the amount of heat transferred to 0.0096 cal. This outcome is essentially in agreement with earlier tests of our own and with later work of W. P. White, who has made a very thorough and careful study of this matter.[4]

The adjustment of temperature between the contents of the gold bottle and the surrounding water in the calorimeter was also tested. Naturally, this adjustment was found to be slow when the contents of the bottle were not stirred; but it was completely accomplished within 5 minutes when they were moderately agitated. The evolution of hydrogen provides sufficient stirring at first; at the end of the reaction the final equalization of temperature was accomplished by stirring with the cap beneath the stopper, which was lowered into the liquid of the bottle. Doubtless the hydrogen rising through the liquid develops a trace of heat through friction, but this must be so small as to be negligible.

The specific heats of both the hydrochloric acid and the cadmium solution (after the experiment) were roughly determined, in the apparatus used in the case of thallium amalgams.[5] This apparatus was standardized by pure water. Exactly 40.00 g. of each liquid was taken for each trial and a definite potential was established at the terminals of the heating resistance for varying lengths of time, producing various rises of temperature in the several liquids. The averages of many trials showed that 480.0 seconds with pure water produced a rise of 4.281°, 360.0 seconds with the cadmium solution produced a rise of 4.167°, and 390.0 seconds with the hydrochloric acid ($HCl.10.05H_2O$) produced a rise of 4.492°. Since the heat capacity of the apparatus was 3.68 cal. per degree, and since the specific heat varies directly as the time and inversely as the temperature increment, the cadmium solution evidently had a specific heat of 0.745 and the hydrochloric acid a specific heat of 0.753. Although these values do not pretend to be very exact, they serve the present purpose. The latter value is consistent with earlier experiments and calculations.[6] The zinc chloride solution mentioned early in this paper was similarly found to have the specific heat 0.864. These specific heats were used in calculating the thermal output of the appropriate reactions.

After a few further preliminary trials with cadmium, four final determinations were made, in each of which (on the average) 169.73 g. of hydrochloric acid (of concentration $HCl.10.05H_2O$, sp. heat 0.753) was used in the gold bottle; 11.024 g. of pure electrolytic cadmium was placed in the stopper and later dissolved in the acid; 0.3 g. of a solution of chloroplatinic acid was added in each case. The flask was surrounded by 799.93 g. of water in the outer platinum vessel. The platinum and gold apparatus and thermometer as before had a total heat capacity of 20.5 and the correction for half the heat capacity of the moist hydrogen

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[4] White, *Phys. Rev.*, **7,** 682 (1916).

[5] Richards and Daniels, THIS JOURNAL, **41,** 1732 (1919).

[6] Ref. 3, p. 1631.

evolved was 0.4, so that the heat capacity of the system was 948.7. There were small deviations from these values in individual cases, but in no case was the deviation enough to produce a significant effect upon the results. Even considerable variations would not have vitiated the exact use of the averages in connection with *average* values in the tables below. The last column of the table gives the products of the values in the preceding column multiplied by 948.7.

TABLE I

SOLUTION OF 11.024 G. OF CADMIUM IN 189.73 G. OF $HCl.10.05H_2O$

| Expt. | $t_1$ | $t_2$ | $t_2 - t_1$ | Stirring correction | $\Delta t$ corrected | Heat evolved |
|---|---|---|---|---|---|---|
| | °C. | °C. | °C. | °C. | °C. | Cal. (19°) |
| 1 | 17.929 | 19.896 | 1.967 | −0.002 | 1.965 | 1,864 |
| 2 | 18.062 | 20.033 | 1.971 | −0.001 | 1.970 | 1,869 |
| 3 | 17.744 | 19.708 | 1.964 | −0.002 | 1.962 | 1,861 |
| 4 | 17.450 | 19.420 | 1.970 | −0.002 | 1.968 | 1,867 |
| Av. | | 19.77 | | | 1.9662 | 1,865 |

On the average 48 mg. of platinum was deposited in each experiment, (0.039 in the form of powder as well as 0.009 upon the gold vessels, as determined by the increase in their weight). From the value 1,865 cal. must therefore be subtracted 18 cal., since it has been shown[7] that every gram atom of platinum precipitated evolves in the process 73 Cal. more heat than the evolution of the equivalent amount of hydrogen. This leaves 1,847 cal., corresponding to the given amount of metal, or 18,832 cal. corresponding to 112.40 g. (the gram atom) of cadmium. In 20° Calories this value becomes 18.838. This value, 18.838 Cal., is the heat of the main reaction concerned: the solution of cadmium at 19.77° in a fairly concentrated acid, present in considerable excess (7.956 mol per gram atom of metal). The result is uncorrected for loss of heat from evaporation of water and for the work done (against the atmosphere) by the moist hydrogen. At 20° it would be 18.822 Cal. (as explained later) since the change of heat capacity is 71 cal./$t$°.

To find the heat of reaction of cadmium on an exactly equivalent amount of hydrochloric acid in dilute solution, this value just given must, of course, be corrected for the heats of dilution of factors and products. The heat of dilution of $HCl.10.00H_2O$ to $200H_2O$ is known, being 1161 cal. per mol.[8] The curve showing heats of dilution at various concentrations shows that this quantity with moderate concentrations is nearly a simple linear function of the concentration,[3] hence the heat of the reaction $HCl.10.05H_2O + 189.95H_2O = HCl.200H_2O$ is 1155 cal. Since 7.956 mols of hydrogen chloride was used per gram atom of cadmium, the

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[7] Richards and Burgess, Ref. 1, p. 454.

[8] Richards, Rowe and Burgess, Ref. 1, p. 1178.

heat of dilution to be subtracted on this account is 7.956 × 1.155 = 9.189 Cal.

With the same apparatus as that used to obtain this datum, we determined the heat of dilution of the product of the reaction, diluting 63.96 g. of the acid cadmium chloride solution to the equivalent extent with 943.6 g. of water, in five successive independent trials. The five experiments had final temperatures averaging 19.75°, and yielded the values 0.253°, 0.255°, 0.253°, 0.252°, and 0.254°, averaging 0.2534°, for the temperature increment on dilution. The heat capacity of the cadmium solution was 47.5 (since its specific heat had been found to be 0.745) and the apparatus had a capacity of 15.1. Hence the total heat capacity warmed in these dilutions was 1,006.3 cal. per degree; therefore the heat evolved was 0.2550 Cal. Multiplying this result by 2.821 × 10.196 to reduce to the equivalent of a gram atom of cadmium, the heat value for the dilution of the total resulting solution containing exactly a gram atom of cadmium is found to be 7.336 Cal. (at 19.75°). Corrected to 20° this becomes 7.365 Cal.[9] Hence the heat of reaction of cadmium on the exactly equivalent amount of $HCl.200H_2O$, evolving moist hydrogen under constant pressure, would be 18.822 − 9.189 + 7.365 = 17.00 Cal. The average heat of evaporation of the water carried away by the hydrogen between the temperature 17.8° and 19.75° would be for a gram molecule of hydrogen 234 cal. Adding this quantity the final expression is obtained.

$$Cd + 2\,HCl.200H_2O = CdCl_2.400H_2O + (H_2)_p + 17.23\text{ Cal.}$$

This result, 17.23, (72.0 kj.) is almost identical with that (17.2) found in the preliminary work. The close agreement is partly accidental, since the earlier result had a large possible error. Even the present value 17.23 has a greater range of possible experimental error than the result with zinc, since cadmium requires moderately concentrated hydrochloric acid for solution, and the heats of dilution of factors and products are therefore necessarily rather large. In the present case an error of 0.001° would cause an error of 0.05% in the main reaction, of 0.3% in the heat of dilution of hydrochloric acid and of 0.4% in the heat of dilution of the product of the reaction. If all these errors should happen to tend in the same direction (which is, of course, unlikely) the error of the final result would be 0.07 Cal. Thus when the heat evolved on dilution is large, as in the present case, these temperature changes should be measured much more accurately than that of the main reaction. It is hoped that the recent gains in accuracy in thermometric measurement may make possible in the near future a closer evaluation of these quantities, leading perhaps to slight revision of the value just given. For the present, however,

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[9] On the fairly safe assumption that the change of heat capacity of this solution is nearly the same as that of hydrochloric acid of that concentration. (See Ref. 3).

this value seems to be more trustworthy than any other which has been published and therefore, even though somewhat tentative, is worthy of record. Calculated to correspond strictly with the isothermal reaction at 20° (the hydrogen being evolved moist from the very dilute acid solution), the value becomes 16.98.

Thomsen's value, 17.6, was distinctly too large, whereas his value for zinc was distinctly too small. This difference in sign of the error is dependent upon the fact that although the dilution of zinc chloride gives out much more heat than the dilution of the equivalent concentration of hydrochloric acid, on the other hand, the dilution of cadmium chloride gives out less heat than the dilution of the equivalent amount of hydrochloric acid. The heats of dilution of the metallic chloride solutions were entirely overlooked by Thomsen.

The temperature coefficient of this heat of reaction cannot be exactly computed with the data at hand. However, since the heat capacity of the contents of the gold flask (together with the hydrogen) increased about 7. cal. per degree during the main reaction, the temperature coefficient of the heat of reaction of a gram atom of cadmium upon excess of hydrochloric acid (4 times the stoichiometric amount of $HCl.10H_2O$) in this way must be about −71 cal. per degree. This is not far from the temperature coefficient of the heat of the corresponding zinc reaction, −74 cal. per degree, although the conditions were not exactly the same, the acid having been less concentrated and in smaller excess in the case of the zinc. Probably even in dilute solutions there is a gain of heat capacity in dissolving cadmium in hydrochloric acid, as in the case of zinc; and theoretical conclusions point to a similar temperature coefficient of the heat of the dilute reaction amounting, perhaps to about −30 cal. per degree.

The correction for the work done by the hydrogen evolved is, of course, identical with that in the case of zinc at the same temperature. Therefore the total energy change $(U) = 17.81$ Cal. or 74.4 kj. at 20°.

The earlier work (of Burgess and one of us) on magnesium needs no revision of this kind, since the acid was diluted in the first place; but the cases of iron and aluminum await further study.

We are indebted once more to the Carnegie Institution of Washington, as well as to an anonymous benefactor of this Laboratory, for generous financial support in this investigation.

## Summary

1. With the apparatus recently described in the case of zinc, the heat of reaction $Cd + 2HCl.200H_2O = CdCl_2.400H_2O + (H_2)_p$ is found to be 17.23 Cal. (or 72.0 kj.) at 20° if the hydrogen is dry; and 16.98 Cal. (or 71.0 kj.) if the hydrogen is moist, (at 20.0° and 760 mm.).

2. The total energy change, $U$, of the reaction is therefore 17.81 Cal. (or 74.4 kj.) at 20°.

3. The specific heats of factors and products and the heat of dilution of the product needful for the attainment of these results were found experimentally.

4. The temperature coefficient of the heat of solution of cadmium in conc. hydrochloric acid is shown to be negative, −71 cal. per degree; probably even with dilute acid it amounts to as much as −30 cal. per degree.

Cambridge 38, Massachusetts

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[Contribution from the Gates Chemical Laboratory of the California Institute of Technology, No. 13]

# THE CRYSTAL STRUCTURE OF AMMONIUM FLUOSILICATE

By Richard M. Bozorth[1]

Received March 22, 1922

## 1. Introduction

Ammonium fluosilicate, $(NH_4)_2SiF_6$, exists in two crystalline forms,[2] cubic and hexagonal. The cubic form is the stable one at ordinary temperatures, while the hexagonal form has been obtained[3] below 5°. It seemed probable that the cubic form has the same structure as ammonium chloroplatinate studied by Wyckoff and Posnjak,[4] and ammonium and potassium chlorostannate studied by Dickinson;[5] but complete evidence of iso-morphism was lacking.[6] It was therefore desirable to study its crystal structure, not only to determine whether it is the same as that of these other salts, but also to measure the size of the unit of structure and the distances between the centers of the various atoms.

Crystals of the fluosilicate were prepared by the spontaneous evaporation at room temperature of an aqueous solution containing an excess of hydrofluoric acid.

The methods employed for obtaining the X-ray data and for the interpretation of these data are essentially those used by Wyckoff and Posnjak and by Dickinson, to whose articles reference may be made for more detailed information.

I wish to express my thanks to Dr. R. G. Dickinson for valuable advice during the progress of this research.

## 2. Determination of the Size of the Unit-cube and the Number of Molecules in It

Photographs of line spectra from the (111) face of a crystal showed

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[1] DuPont Fellow in Chemistry.

[2] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1906**, vol. 1, p. 485.

[3] Gossner, *Z. Kryst. Mineral.*, **38**, 147 (1904).

[4] Wyckoff and Posnjak, This Journal, **43**, 2292 (1921).

[5] Dickinson, *ibid.*, **44**, 276 (1922).

[6] Ref. 2, p. 466.