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# Heat of Solution of Zinc Oxide in 2 *N* Hydrochloric Acid

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The heat of solution of ZnO in 2 *N* hydrochloric acid was found to vary from 185 to 203 calories per gram, depending on the proportion of ZnO. For 1 gram of ZnO in 640 grams of 2 *N* hydrochloric acid, the heat of solution was found to be 185 calories per gram, in fair agreement with the value[2] of 196 calories per gram calculated from the published heats of formation of ZnO, $ZnCl_2$(aq), and HCl(aq), and the measured heat of mixing of $ZnCl_2$(aq) with HCl(aq).

## I. Introduction

Zinc oxide has been found to be a convenient material for determining the energy equivalent (heat capacity) of calorimeters that are to be used for the determination of the heats of solution of acid-soluble materials [1, 2].[1] It has proved to be particularly useful in those laboratories that do not have the relatively elaborate equipment necessary for an electrical calibration.

In the Federal and in the ASTM specifications for measuring the heat of hydration of portland cement, [3, 4], zinc oxide serves as a standard to determine the energy equivalent of the heat-of-solution calormieter. In the specified procedure, 2 *N* nitric acid solution constitutes 98 percent of the solvent, the remaining 2 percent being hydrofluoric acid. The experimentally determined heat of solution of ZnO in this solvent and the value of the heat of solution of ZnO in 2 *N* nitric acid calculated from available heat-of-formation data are in good agreement.

Some investigators, however, have used hydrochloric acid as a solvent in the determination of the heat of solution of portland cement and other materials [2, 5, 6, 7]. In some investigations of this type at this Bureau, zinc oxide has been used to calibrate the heat-of-solution calorimeters.

The data presented here show fair agreement with the value of the heat of solution of ZnO calculated from published heat-of-formation data, when the heat of mixing of $ZnCl_2$ (aq) with HCl (aq) is taken into account.

## II. Apparatus and Reagents

All the determinations were made in a heat-of-solution colorimeter described previously [11]. The energy equivalent of the calorimeter was determined electrically. In each experiment, the calorimeter charge was 640 g of 2 *N* hydrocholoric acid (HCl.26.64 $H_2O$ at 25° C).

Zinc oxide of analytical reagent quality was ground to pass a No. 100 sieve, heated for 1 hour at 900° to 950° C, and stored in the laboratory in a dark screw-capped bottle.

For the determination of the heat of dilution of $ZnCl_2$ in 2 *N* HCl, an aqueous stock solution of $ZnCl_2$, 53.28 $H_2O$ was prepared from $ZnCl_2$ of analytical reagent quality and of known moisture content. The calorimeter sample was taken from this aqueous solution of $ZnCl_2$.

In order to know accurately the temperature of the calorimeter sample, in the dilution experiments, the $ZnCl_2$ solution was kept in a bottle immersed in the constant-temperature bath of the calorimeter. The pipette with which the sample was transferred to the calorimeter was also kept in the bath in a vertical brass tube closed at the bottom and projecting slightly above the water surface. Thus the temperature of the zinc chloride solution was nearly the same as that of the bath. As the calorimeter was operated so that the final temperature was nearly the same as that of the bath, only a small correction was necessary to account for the heat capacity of the sample.

The final temperatures of the calorimeter in the heat-of-solution experiments were from 24.5° to 27.4° C. No attempt was made to correct the heats of solution to 25° C.

## III. Results and Discussion

### 1. Experimental Measurements

Determinations were made of the heat of solution in 2.00 *N* HCl of samples of ZnO ranging from 0.1 to 20 g in weight. Three determinations were made with each size of sample (see table 1). The results were plotted against sample weight, and a line was fitted to the data by the method of least squares (fig. 1). The equation of this line was found to be $Q=184.7+0.91x$, where $Q$ is the heat of solution in calories per gram, and $x$ is the sample weight in grams.

TABLE 1. *Effect of sample weight on the heat of solution of* ZnO *in 640 grams of 2 N* HCl.

| ZnO | Heat of solution | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | Average |
| *g* | *cal/g* | *cal/g* | *cal/g* | *cal/g* |
| 0.1 | 185.4 | 184.6 | 184.5 | 184.8 |
| .5 | 186.4 | 183.9 | 184.6 | 185.0 |
| 1 | 185.0 | 185.4 | 184.4 | 184.9 |
| 2 | 188.4 | 186.7 | 185.8 | 187.0 |
| 3 | 187.0 | 188.7 | 188.1 | 187.9 |
| 4 | 189.4 | 186.7 | 189.8 | 188.6 |
| 7 | 190.9 | 190.7 | 191.7 | 191.1 |
| 10 | 195.0 | 195.3 | 192.7 | 194.3 |
| 14 | 198.1 | 197.1 | 194.1 | 196.4 |
| 20 | 206.6 | 202.6 | 200.8 | 203.3 |

[1] Figures in brackets indicate the literature references at the end of this paper.

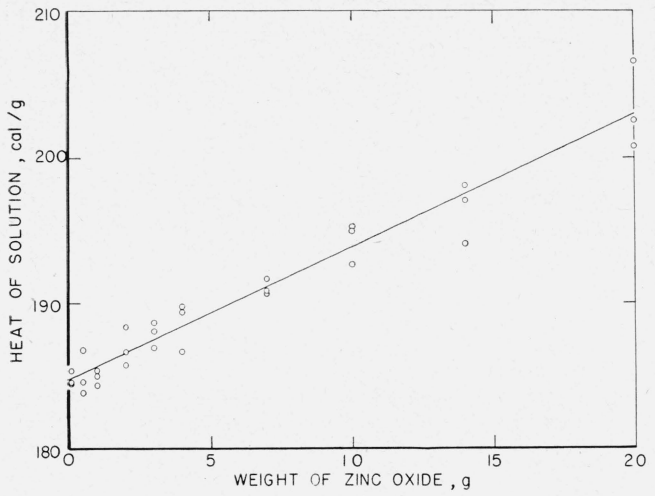


FIGURE 1. *Effect of sample weight on the heat of solution of ZnO in 640 g of 2 N hydrochloric acid.*

The equation of the line is $Q=184.7+0.91x$, where $Q$ is the heat of solution in calories per gram, and $x$ is the weight of the sample in grams.

A sample of 28 g was dissolved, and a value only slightly greater than that of a 20-g sample was obtained, indicating that at higher concentrations, the curve flattens out. An attempt to determine the heat of solution of a 56-g sample failed because of the extreme difficulty in measuring the large and rapid temperature rise, and because the sample would not dissolve completely within a reasonable time, that is, 60 min.

It may be seen in figure 1 that the value of the heat of solution of ZnO in 2 N HCl at infinite dilution is approximately 185 cal/g.

The variation of $Q$ with sample weight, as indicated by the slope of the line in figure 1, is a measure of the change in the heat of dilution for a solution of zinc chloride in hydrochloric acid. The variation of $Q$ also includes the heat of dilution of the hydrochloric acid mix resulting from the formation of water and the removal of HCl as a consequence of the reaction. This heat effect is small relative to the dilution of the zinc chloride solution, except in the case where large samples of zinc oxide are used, in which cases the proportions of HCl removed and of additional $H_2O$ added to the final concentration by the reaction are significant.

## 2. Method of Calculation

The heat of solution of a 1-g sample of ZnO in 640 g of 2.00 $N$ hydrochloric acid at 25° C may be represented by the following over-all reaction

$$\frac{1}{81.38}\mathrm{ZnO}\,(c)+\frac{45.18}{36.46}\mathrm{HCl},\frac{594.82}{18.02}\mathrm{H_2O}\rightarrow\frac{1}{81.38}\mathrm{ZnCl_2},\left(\frac{45.18}{36.46}-\frac{2}{81.38}\right)\mathrm{HCl},\left(\frac{594.28}{18.02}+\frac{1}{81.38}\right)\mathrm{H_2O}+Q.$$

Writing this equation in the customary form based on 1 mole of ZnO

$$\mathrm{ZnO}\,(c)+100.85(\mathrm{HCl},\,26.64\ \mathrm{H_2O})\rightarrow \mathrm{ZnCl_2}\,[98.85\ (\mathrm{HCl},\,27.19\ \mathrm{H_2O})]+Q. \quad (1)$$

Equation 1 may be considered as the sum of the following four equations:

$$100.85\ (\mathrm{HCl},\,26.64\ \mathrm{H_2O})\rightarrow 98.85\ (\mathrm{HCl},\,26.64\ \mathrm{H_2O})+2\ (\mathrm{HCl},\,26.64\ \mathrm{H_2O})+Q_1. \quad (2)$$

$$\mathrm{ZnO}\,(c)+2\ (\mathrm{HCl},\,26.64\ \mathrm{H_2O})\rightarrow \mathrm{ZnCl_2},\,53.28\ \mathrm{H_2O}+\mathrm{H_2O}\,(l)+Q_2. \quad (3)$$

$$\mathrm{ZnCl_2},\,53.28\ \mathrm{H_2O}+98.85\ (\mathrm{HCl},\,26.64\ \mathrm{H_2O})\rightarrow \mathrm{ZnCl_2}\,[98.85\ (\mathrm{HCl},\,27.18\ \mathrm{H_2O})]+Q_3. \quad (4)$$

$$\mathrm{ZnCl_2}\,[98.85\ (\mathrm{HCl},\,27.18\ \mathrm{H_2O})]+\mathrm{H_2O}\,(l)\rightarrow \mathrm{ZnCl_2}\,[98.85\ (\mathrm{HCl},\,27.19\ \mathrm{H_2O})]+Q_4. \quad (5)$$

The heat of the reaction $Q$[2] is the sum of $Q_1$, $Q_2$, $Q_3$, and $Q_4$ and may be calculated if the individual heats of reaction are known. The value of $Q_1$ is zero. The heat of reaction $Q_2$ (eq 3), calculated from heats of formation [8, 9] is 19.11 kcal/mole of ZnO at 25° C.

The value of $Q_3$ (eq 4) was found in the heat of dilution experiments with $ZnCl_2$ to be $-3.22\pm0.01$ kcal/mole.

The value of $Q_4$ (eq 5) was calculated from published data on the heat of dilution of HCl [10], assuming that the heat effect of adding 1 mole of $H_2O$ to a solution of 98.85 moles of HCl and 2,688 moles of $H_2O$ would not be appreciably affected by the presence of 1 mole of $ZnCl_2$ in the solution. The value of $Q_4$ was found to be $+0.02$ kcal/mole.

Thus the heat of reaction $Q$ can be calculated to be

$$Q=19.11-3.22+0.02=+15.91\ \text{kcal/mole}$$
$$=195.5\ \text{cal/g ZnO}.$$

This value differs by 10 cal/g from the value determined experimentally. Part of the discrepancy may lie in the uncertainties in the published heat-of-formation data used to calculate $Q_2$ (eq 3).

The value of the heat of solution of ZnO in 2 $N$ nitric acid was calculated on the assumption that the $Zn(NO_3)_2$ formed is diluted in water, instead of nitric acid, as is actually the case. This value does not differ appreciably from the value determined in this laboratory in experiments in which ZnO was dissolved in a mixture of 98 percent of 2 $N$ nitric and 2 percent of hydrofluoric acids [12]. However, because of the large endothermic heat effect of the dilution of $ZnCl_2$ in HCl, a corresponding assumption in the case of ZnO dissolving in HCl leads to a great discrepancy (100 cal/g) between the value experimentally determined and the value calculated in this manner.

[2] The heat of the reaction is considered to be positive if heat is evolved, i. e., $Q=-\Delta H$.

## IV. Summary

The change of the heat of solution of ZnO in 640 g of 2 $N$ HCl with sample weight was investigated in the range from 0.1 to 20 g of ZnO. This relation can be represented by a straight line having a slope of approximately 1 cal/g/g and an intercept on the $Q$ axis ($Q$ at infinite dilution) of approximately 185 cal/g. For 1 gram of ZnO in 640 g of 2 $N$ hydrochloric acid, the heat of solution was found to be 185 cal/g, in fair agreement with the value of 196 cal/g calculated from the published heats of formation of ZnO, $ZnCl_2$(aq), and HCl(aq) and the measured heat of mixing of $ZnCl_2$(aq) with HCl(aq).

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