[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

THE HEAT OF FORMATION OF ZINC OXIDE

BY GEORGE S. PARKS, CHARLES E. HABLUTZEL AND LAWRENCE E. WEBSTER

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The data in the literature for the heat of formation of zinc oxide are extremely discordant. Thus Mellor[1] gives ten values ranging from 86,900 cal. (Andrews, 1852) to 82,970 cal. (the lowest result of de Forcrand, 1902). Of these the results of de Forcrand are the latest and probably the most reliable. More recently Parr and Moose[2] have reported the value 84,900 cal., obtained by direct combination of the elements, and Maier and Ralston[3] have calculated the values, 82,830 and 83,097 cal., from equilibria measurements and from thermal data, respectively. In view of this situation the present investigation was undertaken.

Richards and Burgess[4] have determined the heat of solution of zinc in hydrochloric acid. In the present case we have measured the heat of solution of zinc oxide under precisely comparable conditions. These two heats of solution, combined with the heat of formation of water, serve as a basis for the calculation of a very reliable value for the heat of formation of zinc oxide from its elements.

Experimental Part

Richards and Burgess in their experiments dissolved 7.5 g. of zinc in 941.4 g. of hydrochloric acid of the strength $1HCl{-}20H_2O$ (approximately 2.633 *N*). We accordingly prepared acid of this concentration and in six series of determinations measured the heat effect observed when 25.83 g. of zinc oxide was dissolved in 2605 g. of acid. Thus the resulting solutions in our experiments had the same concentration of hydrochloric acid and zinc chloride as those obtained by Richards and Burgess.

As a calorimeter for the measurement of the heat of solution we used a Pyrex Dewar jar of 3 liters' capacity, for which a thin cover of cork, coated with paraffin, was made. Three small holes were punched in this cover for the stirrer, for the Beckmann thermometer and for the introduction of the zinc oxide. The glass stirrer was of the propeller type, with eight blades, and gave adequate circulation when operated at about 200 r.p.m. The Beckmann thermometer had been calibrated by the United States Bureau of Standards immediately before the measurements. The heat capacity of the apparatus as a whole was measured first in a series of nine determinations by an electrical method and subsequently in a series

[1] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, **1923**, vol. 4, p. 512.

[2] Parr and Moose, THIS JOURNAL, **46**, 2660 (1924).

[3] Maier and Ralston, *ibid.*, **48**, 371 (1926).

[4] Richards and Burgess, *ibid.*, **32**, 431 (1910).

of five determinations by a rough method of mixtures, the respective mean results being 182 and 185 calories per degree. Accordingly we have used 183 calories in our calculations. For the specific heat of the acid the value of Richards and Rowe,[5] 0.8486 cal./g., was assumed.

In some preliminary experiments with our apparatus it was found that a small part of the oxide had a tendency to cake at the bottom of the Dewar jar and thereby took considerable time to go into solution. This difficulty seemed to be due entirely to the shape of the bottom of the jar and was remedied by introducing about a kilogram of mercury into the container. The mercury took no part in the reaction[6] and, as its specific heat was known, a correction of about 36 calories per degree was added to the heat capacity of the apparatus as previously found. Under these conditions the 25.83 g. of zinc oxide went into solution within a period of five minutes, with a temperature rise of about two degrees above the initial temperature, 18.0°. The Regnault-Pfaundler method was employed in determining the cooling corrections during the solution process and the usual calorimetric precautions were observed throughout the measurements. The reproducibility of the results thus obtained is illustrated by the fact that the nine consecutive runs on Sample I showed an average deviation of 15 calories (0.10%) from the mean value, the maximum deviation being 35 calories (0.23%).

The zinc oxide samples were prepared from Baker's C. P. materials, made by the "wet process" and "dry process," respectively. The manufacturer's analyses as well as subsequent analyses made in this Laboratory indicated that the total impurities were much less than 0.1% in all instances. Sample I was "wet-process" oxide which had been dried on a hot-plate at about 110° for 24 hours. Samples II and III were a similar material which had been heated for 24 hours in an electric furnace at 500° and 800–1000°, respectively. This process of heating at high temperatures caused considerable shrinkage in the apparent volume of the oxide. Sample IV was "dry-process" oxide which had been dried on a hot-plate at 110° for 24 hours and Sample V was similar material heated at 500° for 12 hours. These last two samples occupied a larger volume per gram and apparently were much more finely divided than the corresponding ones prepared from the wet-process product. Sample VI was "recrystallized" oxide, made by sealing dry-process material into an evacuated (0.01 mm.) silica flask and heating to approximately 1100° for about 60 hours.[7]

The following table summarizes our results for the heat of solution of these six samples of zinc oxide in acid of the strength $1HCl–20H_2O$. The data are expressed in terms of the 18° calorie for a final temperature of 20.0°.

[5] Richards and Rowe, *Proc. Am. Acad. Arts Sci.*, **43**, 475 (1908).

[6] As a matter of fact, in a number of determinations, including about half of those in Series IV, the mercury was omitted. The results obtained in these cases showed no essential differences from the others, although a somewhat longer time interval was required for complete solution of the oxide.

[7] Numbers VI and IV were identical with "samples 2 and 3," respectively, employed in some previous heat-capacity determinations (Maier, Parks and Anderson, THIS JOURNAL **48**, 2572 (1926)).

TABLE I

HEAT OF SOLUTION OF ZINC OXIDE IN $1HCl-20H_2O$ HYDROCHLORIC ACID AT 20.0°

Sample	No. of detns.	Mean result, ΔH of solution per mole, Cal.
I	9	−15,280
II	5	−15,281
III	5	−15,280
IV	16	−15,251
V	11	−15,253
VI	1	−15,316

Discussion

The value obtained for Sample VI cannot be considered very reliable, as there was only enough of this material for one determination. Moreover, we regard the results with dry-process oxide as less reliable than those obtained with wet-process oxide, since the former material, being more finely divided, presented greater difficulty in handling and usually required a longer time for complete solution. Therefore, giving the wet-process values greater weight, we have selected —15,275 cal. as the most reliable value for the ΔH of solution of zinc oxide per formula weight. This result is in 18° calories; converted over into 15° calories, it becomes —15,263 cal.

By interpolating in the data of Lewis and Randall, we obtain —68,313 15° cal. for the ΔH of formation of water at 20°. This is the value for the pure liquid, while in the present case we are dealing with water in a solution containing considerable hydrochloric acid and a little zinc chloride. By the methods of Lewis and Randall[8] we have estimated the relative partial molal heat content of water under these conditions to be —28 cal. The corresponding ΔH of formation is then —68,341 cal. The value obtained by Richards and Burgess for the heat of solution of zinc in $1HCl-20H_2O$ at 20° is 30,190 18°-cal. per gram atom. This is equivalent to 30,166 15°-cal. We can now calculate the ΔH of formation of zinc oxide as follows

$$ZnCl_2, \text{aq.} + H_2O = ZnO(s) + 2HCl, \text{aq.}; \ \Delta H = +15{,}263 \text{ cal.}$$
$$H_2(g) + \tfrac{1}{2} O_2(g) = H_2O \text{ (in solution)}; \ \Delta H = -68{,}341 \text{ cal.}$$
$$Zn(s) + 2HCl, \text{aq.} = ZnCl_2, \text{aq.} + H_2(g); \ \Delta H = -30{,}166 \text{ cal.}$$

Adding we have

$$Zn(s) + \tfrac{1}{2} O_2(g) = ZnO(s); \ \Delta H = -83{,}244 \text{ cal.}$$

According to these figures the heat evolved on the formation of a formula weight of zinc oxide from its elements at 20° is in round numbers 83,240 cal. As ΔCp is close to zero, this result will not change appreciably with small changes in temperature. In view of the reliability of the various data employed, we consider it accurate to within 200 cal.

[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, pp. 477, 92 and 96.

De Forcrand,[9] in his determinations of the heat of solution of zinc oxide in acid, used samples of oxide from different sources and thus obtained the following results for the heat of formation:

ZnO prepared	from $Zn(OH)_2$ at 125°	82,970 cal.
	from $Zn(NO_3)_2$ at 350°	83,000 cal.
	from "rouge blanc"	84,300 cal.
	by combustion of zinc	84,700 cal.

He considered that his data showed a progressive "polymerization" or transformation of the zinc oxide at high temperatures but, as Maier and Ralston have pointed out, his determinations were not made upon the same samples prepared at high and low temperatures. Certainly our present results obtained with samples of zinc oxide which have been subjected to varying heat treatment fail to confirm this polymerization theory.

Summary

1. ΔH, the heat absorbed in the reaction, $ZnO(s) + 2HCl(2.63\ N) = H_2O + ZnCl_2$ (the resulting solution being about 2.39 *N* in hydrochloric acid and 0.24 *N* with respect to zinc chloride), has been found to be —15,263 15° cal. at 20°.

2. By combination of this value with the result of Richards and Burgess for the heat of solution of zinc in acid of the same concentration, the heat of formation of zinc oxide from its elements has been calculated to be 83,240 (±200) cal.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE FREEZING POINTS OF AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID[1]

BY HARRIS MARSHALL CHADWELL

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The technique of determining the depression of the freezing point of a solvent by a second chemical substance has improved in two directions since the days of the pioneers in this field. More accurate methods of measuring temperature have been substituted for the mercury thermometer. Thermocouples have been used by Hausrath,[2] Osaka,[3] Jahn,[4]

[9] De Forcrand, *Ann. chim. phys.*, [7] **27**, 38 (1902).

[1] Determinations similar to those reported in this paper were made in 1922 at the Wolcott Gibbs Memorial Laboratory at Harvard University with the collaboration of Professor T. W. Richards. The platinum thermometer used in the earlier experiments was subsequently ruined during standardization. The technique is practically the same as that developed in 1922.

[2] Hausrath, *Ann. Physik*, [4] **9**, 522 (1902).

[3] Osaka, *Z. physik. Chem.*, **41**, 560 (1902).

[4] Jahn, *ibid.*, **59**, 31 (1907).