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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE HEAT OF FORMATION OF ZINC OXIDE[1]

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In spite of the recent careful work of Parks, Hablutzel and Webster[3] on the heat of solution of zinc oxide in hydrochloric acid, the heat of formation of the oxide derivable therefrom by combination with the heat of solution of zinc and the heat of formation of water still remained uncertain by several hundred calories. Parks and co-workers used the results of Richards and Burgess[4] for the solution of zinc, but Richards and Thorvaldson[5] made later determinations in solutions of higher final zinc concentration which differed by 280 calories when brought to comparable conditions of dilution and temperature. This discrepancy is greater than the probable error of available free energy and entropy determinations on zinc oxide.[6,7]

The Pacific Experiment Station of the U. S. Bureau of Mines, in the course of its program of study of the thermodynamic properties of metallurgically important oxides, has carried out redeterminations of the heat of solution of zinc and zinc oxide, in order to arrive at finally acceptable figures. The results, aside from their practical interest with relationship to the metallurgy of zinc, are of some theoretical interest, because they furnish the last link in a comparison of heat of formation, free energy and entropy as derived from widely different experimental methods, and so constitute a direct and many-sided check on the third law of thermodynamics. Although few would now question the utility of this law, it has not as yet attained widespread application to metallurgical processes in this country. The use of the Nernst approximation formula is unsatis-

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[1] Published by the permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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[3] Parks, Hablutzel and Webster, THIS JOURNAL, **49**, 2792 (1927).

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

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

[6] Maier, Parks and Anderson, *ibid.*, **48**, 2564 (1926).

[7] Millar, *ibid.*, **50**, 2653 (1928).

factory for the prediction of even moderately precise reduction equilibrium, and the precise methods of Lewis and Randall have been unavailable to discussions of oxides, because of dearth of data on these materials.

The experiments here described were performed in a calorimeter with some unusual features. Because of the wide variety of determinations included in the originally projected program, an instrument of considerable flexibility was desired. The apparatus was designed and constructed before the appearance of White's[8] catechistical treatise, and it was first proposed to render the calorimetric process both adiabatic and isothermal. Initial experiments showed, however, that Newton's law of cooling for the completed calorimeter was so accurately obeyed that the maintenance of neither of these conditions was essential for precise work when the duration of the experiments did not exceed a few hours.

The Calorimeter

The unusual features of this calorimeter are the use of a specially constructed and calibrated copper resistance thermometer for measurements of temperature; the equipment of the instrument with a special heating coil of manganin, and an ethyl bromide "boiler" for cooling; and the expedient use of tantalum and bakelite for those portions subject to corrosion. The resistance thermometer is described in detail elsewhere.[9] Details of the other arrangements will be evident from the diagram of Fig. 1.

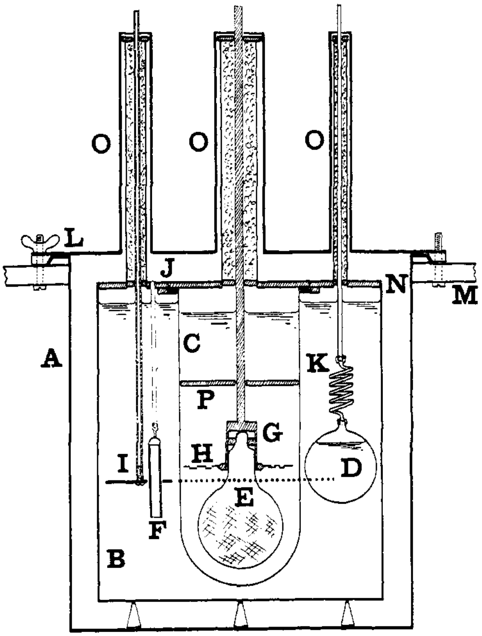

Fig. 1.—The calorimeter.

The outer cylindrical shell A is of heavy sheet copper, heavily gold plated and polished on the inner surface, and is 24 cm. diameter and 26 cm. high. A compression top of similar material has a ground seal at L, and is held in place by twelve screws and wing nuts. From the top extend five copper chimneys O–O–O (three only shown). The calorimeter jar, B, is of 22-gage copper, gold plated and polished externally. It is separated from the shell A by a 2-cm. air space and supported on the bottom by three bakelite cones. A tightly fitting top J is of $^{3}/_{16}$-inch bakelite, and carries bakelite tubing chimneys, which serve as packing glands. Kapok floss, lightly oiled, serves as a nearly frictionless, yet relatively impervious, packing material.

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[8] W. P. White, Am. Chem. Soc. Monograph 42, Chemical Catalog Co., New York, 1928.

[9] Maier, "Resistance Thermometers for Chemists," submitted to *J. Phys. Chem.*, but not yet published.

The mixing chamber, C, is of 10 mil. thick tantalum, with roller welded seams, hemispherical bottom and flanged top. It is suspended from the top by a bakelite ring at J.

Reciprocating stirrers I and H are suspended from bakelite tubes or rods. Three such tubes support the copper ring I, which is slit to prevent inductive effects in the thermometer circuits because of its motion in the earth's magnetic field and to render the stirring more effective by lack of symmetry, and which has ports for passing the resistance thermometer F, the "boiler" D, and the manganin heater not shown, but similar in construction to F. The inner stirring head G is of bakelite, and carries the 25-mil. tantalum stirrer H. The three supporting tubes for I, and the single solid rod carrying G are attached to a specially designed "splashless" reciprocator (not shown), carried by a cross member of the supporting frame M. The actuating cam motion of the reciprocator is of such a type that the velocity at the top of the stroke is a minimum and a maximum at the bottom. The speed is adjustable to 6-, 3- or 2-second cycles, and the stroke is about 5 cm. A bakelite spider P serves as guide for the inner stirrer.

The sample flask E is blown with thin bulb walls, and fixed into the head G with a rubber washer. The attachment of the supporting rod to the reciprocator is a quick release mechanism, enabling the bulb E to be readily smashed against the bottom of the tantalum can while the stirring mechanism is in uninterrupted motion.

The boiler D is of thin-walled pyrex glass, connected by a soldered joint to the helical $^1/_8$-inch copper tube coil K. This coil serves to prevent entrainment of ethyl bromide, and make certain that the vapors issuing from D are at the temperature of the calorimeter. The extension of K through the chimney is of thin glass, with a soldered joint.

The frame M, carrying the reciprocator, is suspended above an oil thermostat by a rack and pinion operated through an irreversible worm drive. Under operating conditions the entire shell is submerged approximately to the O–O–O level.

The joint L is made oil tight with a thin coating of a heavy paste consisting of zinc oxide and glycerin. The top of the jar is sealed at N by winding several thicknesses of electrician's rubber tape about it with considerable tension. The joint at J is sealed by a coating of heavy stopcock grease.

The tantalum and bakelite construction of this calorimeter has proved highly satisfactory. As compared to a gold or platinum calorimeter, the tantalum shows a decided saving in first cost, and its hardness and toughness render it immune to damage by rough treatment. After breaking numerous flasks upon the bottom, the surface was unmarred, nor has there been the slightest trace of corrosion in 2.7 *N* hydrochloric acid after a total time of contact extending over several months. The bakelite, too, has proved to be practically unaffected by the solutions used. Because of plastic flow the bakelite top has become slightly concave, but this could have been avoided by better design, or perhaps a ribbed construction. The ease with which fairly good screw threads may be cut in bakelite, combined with its low thermal conductivity and ability to withstand acid corrosion, commends it highly for calorimetric construction where these properties are desired.

Operation of the Calorimeter

The thermostat in which the calorimeter is submerged is at 25 ± 0.005°. The zero of the resistance thermometer temperature scale is 25.006°, and within satisfactory limits of error the resistance thermometer reading gives the thermal head of heat exchange between calorimeter and surroundings. The total heat capacity of the calorimeter with 5 liters of water in the jar, and 0.6 to 0.8 liter of acid in the can, is between 5500 and

6000 calories per degree, and the Newton's law constant is 0.001° per degree per minute. The rate of heat exchange was a linear function of the thermal head to within 0.5%, so that the uncertainty of determination of heat exchange under unit thermal head for an experiment of 100 minutes' duration is about 0.005°, or 2.5 calories.

Because of the exactness with which the heat exchange rate depends upon the thermal head, the ethyl bromide boiler was used only for adjusting the temperature of the calorimeter in these experiments. The operation of the calorimeter, both adiabatically and isothermally, will be described at a later date. The sequence of operations in these experiments was as follows: (1) determination of initial heat capacity, (2) adjustment of temperature by evaporation of ethyl bromide in preparation for the determination of the heat of solution, (3) determination of heat of dissolution, (4) determination of final heat capacity.

The determination of initial and final heat capacities was accomplished electrically. The manganin heater, previously mentioned as similar in construction to the resistance thermometer, had an accurately determined resistance of 100.034 International ohms, as compared with a standard resistance calibrated by the Bureau of Standards. Energy was obtained from thermally insulated polarized alkaline storage batteries, and the current measured every five minutes by observing the drop across a standardized 0.4-ohm manganin resistance (0.399395 International ohms) (kept in the thermostat) with a White double potentiometer. The energy rate was 1 to 1.5 cal. per second. The heating periods of from one to one and a half hours were measured with a stop-watch which had been compared to an astronomically checked chronometer, and during this period the current variation was less than 1%. If I_n is the current at any reading time $= I_o + \Delta_n$, where I_o is a selected approximately mean value, the average square of the current was taken as $I_o^2 + [\Sigma_o^n(2I_o\Delta_n)]/n$ neglecting the Δ_n^2 terms, and the total energy calculated as $I_{av.}^2\, Rt$, using 4.184 for the conversion factor from International joules to 15° calories. During the experiments the temperature range was held within approximately one degree from the temperature of the surroundings.

After determination of the initial heat contents, the temperature was brought back to a suitable point in preparation for the dissolution experiment, by applying uniform suction to the outer end of *K*. With no appreciable difficulty the external pressure in the line to *K* was maintained constant, resulting in a uniform cooling rate variable from 0 to 1.5 cal. per second.

When the desired temperature (about 24°) had been reached by the contents of the calorimeter, no further evaporation of the bromide was permitted. Thermal equilibrium was attained in four to six minutes. After a preliminary rating period, flask E was smashed at a definite instant and the determination completed in a conventional manner. Points on the temperature curve were plotted on an adequately large scale and the corrected temperature rise was calculated by a graphical Regnault–Pfaundler method. Before the calorimeter was dismantled, the determination of final heat capacity was made. In the calculations correction for the heat content of ethyl bromide evaporated was made at a rate of 0.193, 15° calories per gram, a measured value from experiments to be described elsewhere.

The method of use described above has a number of advantages. Foremost of them is the possibility of direct determination of the temperature coefficient (ΔC_p) of the reaction, a matter of considerable importance in reactions such as the solution of metals or oxides in acid, where the coefficients may be as high as 100 or more calories per degree per formula weight. Moreover, the calibration of the resistance thermometer enters only for the determination of the corrections of heat to a definite temperature; the essential heat determination might be made with a purely arbitrary thermometer scale, that is to say, the direct determination of the electrical energy required to carry the calorimeter and contents through the same temperature rise as that produced by chemical heat. Since random errors in the heat contents determinations are largely magnified in the ΔC_p calculated by difference, the concordance of this quantity per formula weight in a number of duplicate determinations, especially where different quantities of reagents are used, serves as a useful criterion for the authentication of the experimental results. Thus any systematic errors will be ascribable, in a series of determinations showing good concordance in ΔC_p, only to systematic errors in the measurements of electrical energy. In these measurements, repeated checks of the resistances and standard cells used for the electrical measurements showed the uncertainty in energy determinations to be less than one-half per mille.

The Heat of Solution of Zinc Oxide

In the article by Parks and co-workers the statement is made: "Thus the resulting solutions in our experiments had the same concentration of hydrochloric acid and zinc chloride as those obtained by Richards and Burgess." Since water is formed by the action of zinc oxide and acid, but not by metal and acid, it is impossible to have identical initial and final concentrations in the dissolution of oxide and metal, and the authors of the quotation seem to have used identical initial, and not final concentrations. Richards and Burgess dissolved 7.5 g. of zinc in 941.4 g. of hydrochloric acid, 1HCl to $20H_2O$, and in these low concentrations the heat of dilution of the solutions, caused by the formation of water, is not great. Because of the large excess of acid used, the heats of dilution of the zinc-containing solutions will not be markedly different from that of pure hydrochloric acid, and may be estimated by the methods of Lewis and Randall[10] to be 27 calories per gram atom of zinc at these concentrations. In the higher concentrations of Richards and Thorvaldson the effect is much larger and cannot be satisfactorily estimated.

In the experiments here described, the "dry process" zinc oxide used had less than 0.05% of impurity, the chief impurity being traces of water-soluble sulfate. The samples were washed, dried and ignited at 600° to decompose traces of carbonate. A blank heat of wetting determination was made on this material by breaking an evacuated sample bulb containing 41.13 g. of oxide under 850 g. of carbonate-free water in the calorimeter. There resulted a temperature rise of 0.0048°, corresponding to a heat effect of 53 calories per formula weight of ZnO. This heat represents the summation of the heat of wetting of the oxide, the heat to form a saturated solution of oxide in water, and the heat of solution of residual traces of soluble impurities such as sulfate.

No better accuracy than 50 calories per formula weight may, therefore, be claimed for experimental results in which the particle size of zinc oxide is not determined, and since it did not seem practical to separate the various items of heat involved, the following experiments could not be of greater accuracy than this.

TABLE I

SOLUTION OF ZINC OXIDE, RICHARDS AND BURGESS CONCENTRATIONS

	Expt. 1	Expt. 2
Weight of ZnO, g	8.2396	8.4495
Acid 1HCl:20H_2O, g	850	850
Heat capacity of calorimeter, cal	6076.0	5950.4
Uncorrected temperature rise, °C	0.2473	0.2542
Corrected temperature rise, °C	0.2462	0.2571
Final temperature, °C	25.03	25.07
Heat of reaction, cal	1495.1	1529.8
ΔH at final temperature	−14765	−14781
ΔH_{298}	−14769	−14791

Average ΔH_{298}	−14780
Heat of dilution (calcd.)	27
Corrected heat of solution of ZnO	−14753
R. & B. Heat of solution of zinc (dry gas) at 20°	−30166
Correction to 25°	555
Heat of solution of zinc at 25°	−29611
Heat of formation of liquid H_2O (in soln.) at 25°	−68298
Sum	−97909
Heat of solution of ZnO	−14753
Heat of formation of ZnO at 25°	−83156

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[10] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, pp. 92, 96, 477.

In Table I are given the results of two dissolution tests using concentrations similar to those of Richards and Burgess. Through an error, the zinc weighed out in the first experiment was slightly less than should have been used to conform strictly to these concentrations. Because of the relatively low concentration of zinc in the final solution of these first tests, no appreciable error will be introduced because of this. The weights of zinc and acid are reduced to a vacuum basis.

The heat capacities of the calorimeter are 15° calories, and represent the thermal content per degree before the reaction. The heat of reaction calculated, therefore, represents the isothermal heat at the final temperature. Because the dissolution of 8 g. of oxide in 850 g. of acid does not produce a marked total change of heat capacity in this calorimeter, the temperature coefficient of the reaction was calculated rather than determined experimentally as in later experiments. From the data of Richards, Mair and Hall[11] the specific heat of the acid used was estimated to be 0.8528 at 25°, and from these data and those of Richards, Rowe and Burgess[12] that of the resulting zinc chloride solution, 0.8618. Then $\Delta C_p = 858.3 \times 0.8618 - (850 \times 0.8528 + 0.1013 \times 9.65) = 13.7$ calories per degree, or 135 calories per formula weight of ZnO. The figure 9.65 for the molal specific heat of zinc oxide is taken from the results of Millar.

In correcting the heat of solution of zinc given by Richards and Burgess as 30,190, 18° calories at 20 to 25°, the difference in heat capacities of final and initial solutions was taken from the work of Richards, Rowe and Burgess (page 1182) as 9 calories for 5 g. of zinc. When this is corrected for the specific heat of the zinc, $\Delta C_p = 8.5$ or 111 calories per formula weight of zinc.

The heat of formation of liquid water was taken as $\Delta H_{298} = -68{,}270$ from Lewis and Randall, with an additional 28 calories as correction for the relative partial molal heat content of the water in the acid solutions used.

The final result of the experiments for the heat formation of oxide, $\Delta H_{298} = -83{,}156$ calories, compared well with the result of Parks and co-workers, −83,244, although this latter figure would seem to require a correction of 27 calories for the heat of dilution of the solutions creditable to the water formed by the reaction, resulting in −83,271 calories. The agreement is well within the accuracy of 200 calories estimated by Parks. Because the author's results are somewhat lower than Parks', the discrepancy of 280 calories noted between Richards and Burgess' results, and the presumed more accurate results of Richards and Thorvaldson for zinc metal becomes enhanced in the heat of formation of the oxide, and the desirability of determining the heat of solution of the oxide in more concentrated solutions becomes apparent.

The first experiments at the higher concentrations were failures because

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[11] Richards, Mair and Hall, THIS JOURNAL, **51**, 725 (1929).

[12] Richards, Rowe and Burgess, *ibid.*, **32**, 1176 (1910).

of the formation of insoluble oxychlorides. In one case the oxide was stirred for two days in the acid without complete dissolution, and the final product was a rock-hard cake. Many expedients were tried, but the only one which proved effective was to wet the oxide with water before sealing into the bulb E; when this was done the dissolution could be completed in less than one hour. At these concentrations the thermal effect of water formed by the reaction was not calculable, and subsequent experiments were made with a weighed amount of water added to each sample. Since the heat effect of the reaction is independent of the path, the determination of the heat of dilution of a zinc chloride–hydrochloric acid solution, from the concentration used by Richards and Thorvaldson to the final strength obtained in these experiments, enables the effect not only of the added water, but also of the water formed during the reaction, to be determined.

In order to determine this heat of dilution, 665.59 g. of a solution identical in concentration with Richards and Thorvaldson's final was diluted in the calorimeter with 58.61 g. of water, the stoichiometric equivalent of the concentrations used later for the water added to and formed by the zinc oxide. The uncorrected temperature rise was 0.0355°, the corrected, 0.0337° and the final temperature 24.80°. The initial heat capacity of the calorimeter was 5582.2 calories, the final 5602.5, and ΔC_p per formula weight of zinc in solution 39.6 calories per degree. The heat of dilution is then $\Delta H_{298} = -359$ cal.

In Table II are recorded the results of three successful experiments on the dissolution of zinc oxide at the higher concentrations, the final result of which, $\Delta H_{298} = -17{,}280$ calories (corrected for dilution), is to be considered in connection with the data of Richards and Thorvaldson, who gave 32,795 calories at 20° for the reaction giving wet gas, or 33,017 for dry gas. Their temperature coefficient was 74 calories per degree for the wet gas reaction, which with appropriate correction becomes 72.6 calories per degree for the dry. Then the heat of dissolution of zinc at 25°, and at these concentrations, is 32,654, which upon conversion to 15° calories is 32,641. By combination with the author's figure at these concentrations corrected for dilution, and using the same heat of formation of liquid water as before, the heat of formation of zinc oxide at 25° from these data appears to be 83,659, as compared to 83,156 from the previous experiments. The discrepancy of 503 calories between the former figure and that calculated from the results of Richards and Burgess is not readily explainable on any basis except that the measurements of Richards and Thorvaldson were not, in fact, more precise than the earlier data, but rather less so. From the free energy determined by cell measurements, and the entropy from low temperature specific heats, Millar calculated by thermodynamic methods $\Delta H_{298} = -83{,}130 \pm 100$, thus confirming the earlier data, rather than the results obtained in concentrations similar to those of Richards and Thorvaldson.

TABLE II

SOLUTION OF ZINC OXIDE, RICHARDS AND THORVALDSON CONCENTRATIONS

	Expt. 3	Expt. 4	Expt. 5
Weight of ZnO, g.	27.0874	44.3981	54.0857
Moles of ZnO	0.33289	0.54563	0.66469
Weight of acid, 1HCl:$20H_2O$, g.	411.04	673.72	820.73
Weight of water with oxide, g.	32.035	52.535	63.930
Initial heat capacity	5570.1	5759.5	5959.8
Final heat capacity	5608.5	5819.4	6033.3
ΔC_p for the reaction	38.4	59.9	73.5
ΔC_p per formula weight of ZnO	115	110	112
Uncorrected temperature rise, °C	1.0418	1.5684	1.9087
Corrected temperature rise	1.0530	1.6585	1.9571
Final temperature, °C	25.32	26.03	25.81
Heat of reaction	5865.3	9552.1	11663.9
ΔH at final temperature	−17619	−17507	−17508
ΔH_{298} (uncorrected for dilution)	−17656	−17623	−17639

Average, −17639. Heat of dilution, −359. Corrected ΔH_{298} −17280.

Heat of Solution of Zinc

Through the courtesy of the New Jersey Zinc Company a sample of "spectroscopically pure" zinc, containing less than 0.001% impurity was obtained, and its heat of solution was measured at the same concentrations used by Richards and Thorvaldson. Because of the extreme purity of the metal, much difficulty was experienced in dissolving it in the calorimeter. Small amounts of platinic chloride added to the hydrochloric acid accelerated the reaction, but did not give acceptable speed. The metal was finally melted in silica, cast into rods, the oxide-containing skin removed on the lathe, and the inner part turned into a thin curl-like ribbon some 0.005″ thick. A sample of the material was weighed, submerged in a nearly neutral 0.3% platinic chloride solution for a few moments, quickly removed, rinsed and dried with absolute alcohol. From the weight after this treatment the residual mass of zinc was calculable, since the absence of hydrogen evolution indicates stoichiometric replacement. Such material was completely soluble in a half hour's time.

In order to insure saturation of the evolved hydrogen with water vapor and prevent entrainment of solution, bulb E was slightly modified. It was made cylindrical, and had a separate thin, slightly convex bottom attached by rubber tubing. Instead of sealing the top, a small rubber stopper carrying a downward extending glass rod was provided. This rod nearly touched the convex bottom, so that when the bottom was broken, the rod pushed out the stopper. The bakelite head G then served as a bubbler for the gas. The zinc was prevented from issuing from the cylindrical part of the container by means of rather coarse mesh screens of fine platinum wire, held in place by tantalum spring-rings.

Five determinations of the heat of solution of the pure zinc metal in acid concentrations similar to Richards and Thorvaldson's were made, of which the two reported in Table III were completely satisfactory. The first three were made upon unplated zinc, where the action of the acid on the zinc was enhanced in the first by mechanical contact with a platinum wire, and in the next two by the addition of small amounts of platinic chloride solution to the acid. In the first case complete solution required more than four hours' time, and in the following two cases three, and one and one-half hours, respectively. The results obtained were identical with those shown in the table to within ± 125 calories, but are not reproduced in full because they were obviously not completely satisfactory. Large temperature corrections were involved in this time period, and the uncertainty involved in correcting for the platinic chloride added was considerable. The concordance of ΔC_p values in the two completely satisfactory determinations of Table III is taken to indicate that further experiments would not change the results for the materials used.

From data of the "International Critical Tables" the vapor pressure of water above these solutions at the average temperature of Expt. 6 (24.99°) is estimated to be 20.3 mm., the corrected atmospheric pressure being 760.0 mm., including a small hydrostatic pressure on the exit gas. Then 0.001219 mole of water vapor was carried off by the hydrogen; correcting the heat of vaporization of water, 10,450 calories, for the relative partial molal heat content of water in these solutions, 28 calories, the heat absorbed in vaporization is 127.7 calories, or 287 calories per gram atom of zinc. From this the dissolution of zinc to produce dry gas becomes $\Delta H_{298} = -32{,}190$, as compared to $-32{,}654$ calculated from Richards and Thorvaldson, and the heat of formation of zinc oxide from the author's results is then $\Delta H_{298} = -83{,}208$. This final figure differs by but 50 calories from the results obtained using Richards and Burgess' heat of solution of zinc, and it seems certain that Richards' earlier results were the more accurate. The difference between

TABLE III

SOLUTION OF ZINC METAL, RICHARDS AND THORVALDSON CONCENTRATIONS

	Expt. 6	Expt. 7
Weight of zinc, g.	29.0737	29.9701
Gram atoms of zinc	0.44476	0.45847
Weight of acid, 1HCl:20H_2O, g	549.17	565.70
Initial heat capacity	5630.2	5658.7
Final heat capacity	5663.3	5692.8
ΔC_p for the reaction	33.1	34.1
ΔC_p per gram atom of zinc	74.4	74.5
Uncorrected temperature rise, °C.	2.3971	2.5561
Corrected temperature rise	2.5127	2.5816
Final temperature, °C.	26.19	25.63
Heat of the reaction	14147	14608
ΔH at final temperature	−31807	−31862
ΔH_{298} (moist gas)	−31896	−31909

the dissolution of wet and dry oxide as estimated from the blank experiment was shown to be 53 calories, and if this correction be applied to the results of Expts. 1 and 2, which were performed with dry oxide, the heat of formation of wet oxide from these experiments becomes $\Delta H_{298} = -83{,}212$. The concordance is probably fortuitous, and no accuracy better than 50 calories is claimed.

In the above calculations, the heat of formation of liquid water has been taken from Lewis and Randall as $\Delta H_{298} = -68{,}270$, but Roth has given as a more probable figure $\Delta H_{298} = -68{,}330$.[13] If this latter figure is accepted, the heat of formation of zinc oxide becomes $\Delta H = -83{,}270 \pm 50$.

Conclusion

Except for the work of Parks discussed above, recent thermochemical determinations of the heat of formation of zinc oxide are limited to the experiments of Roth and Chall,[14] who worked at 50°, and obtained results varying from 82,825 to 82,905 calories per formula weight. W. Biltz and Wagner[15] and Biltz and Hohorst[16] determined the heat of solution of metallic zinc in hydrochloric acid, but their results cannot be regarded as significant for the determination of the heat of formation of oxide. By a curiously elliptic process of reasoning, these investigators first determined the water equivalent of their calorimeter by the use of Richards and Burgess' heat of solution of zinc, then gave the heat of solution of zinc obtained from slightly different quantities of metal, differing from Richards by more than 100 calories.

None of the previous investigators seem to have been much at pains to correct their results for the temperature coefficients of the reaction, with the exception of Richards and Burgess and Richards and Thorvaldson. These coefficients are seen from the data given above to be more than 100 calories per formula weight per degree for the solution of oxide, and may result in corrections of several hundred calories in actual cases. In the present work such corrections have been made, as well as those resulting from heats of dilution.

Summary

A calorimeter of some unusual features, including the use of tantalum, bakelite, cooling and heating devices, and a precision resistance thermometer, is described.

The heats of solution of zinc oxide and zinc metal have been redetermined, and the result agree with the earlier work of Richards and Burgess on the metal, rather than the later results of Richards and Thorvaldson.

[13] Landolt-Börnstein, 5th ed., 1st Ergänzungsband, **1927**, p. 829.

[14] Roth and Chall, *Z. Elektrochem.*, **34**, 185 (1928).

[15] Biltz and Wagner, *Z. anorg. allgem. Chem.*, **134**, 10 (1924).

[16] Biltz and Hohorst, *ibid.*, **121**, 16 (1922).

The figure for zinc oxide $\Delta H_{298} = -83{,}270 \pm 50$ (15° calories) is proposed as most acceptable on the basis of experimental work now available. The probable uncertainty of about 50 calories is nearly the same as may be inherent in the heats of formation of water as used. The experimental results confirm estimates by thermodynamic methods.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE ADSORPTION OF WATER AND BENZENE VAPORS BY MANGANESE DIOXIDE[1]

BY H. W. FOOTE AND J. K. DIXON

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Manganese dioxide is an active catalyst for the oxidation of carbon monoxide. Bray and his students[2] have made a very complete investigation of the properties of copper oxide–manganese dioxide catalysts. Bray and Draper[3] have determined water isotherms for these oxide mixtures at 25° and showed how these vapor isotherms could be used in determining the structure of the oxides. Whitesell and Frazer[4] have developed a method for preparing manganese dioxide, yielding a product which is a more active catalyst than the mixtures with other oxides. The present investigation deals with the adsorption of water and benzene by manganese dioxide prepared according to this method. The effects on the adsorption isotherms of temperature, temperature of outgassing, and the presence of permanent gases have been investigated and the results have been used to draw some conclusions with regard to the structure of the oxide and the mechanism of the adsorption process.

Materials

The manganese dioxide used in the adsorption isotherms was prepared by sifting finely powdered c. p. potassium permanganate into concentrated nitric acid, according to the method of Whitesell and Frazer.[4] The suspension was stirred by a motor at a temperature of 25–30°. After complete reaction, the oxide was allowed to settle, then filtered and washed until the filtrate showed no test for nitrates. The product was dried for seventy-two hours at 110–115°. The product was then further washed by decantation and on the filter for a week. Different lots of this material were heated

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[1] An abstract of a dissertation presented by J. K. Dixon to the Graduate School, Yale University, 1929, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Almquist and Bray, THIS JOURNAL, **45**, 2305 (1923); Hoskins and Bray, *ibid.*, **48**, 1454 (1926); Bray and Doss, *ibid.*, **48**, 2060 (1926).

[3] Bray and Draper, *Proc. Nat. Acad. Sci.*, **12**, 295 (1926); Draper, THIS JOURNAL, **50**, 2637 (1928).

[4] Whitesell and Frazer, *ibid.*, **45**, 2841 (1923).