Summary

The influence of water on the halogen-hydrogen combinations is discussed. Reasons are advanced for the hypothesis that the primary chemical reaction takes place between halogen atoms and hydrogen. Halogen molecules excited either by light in the visible portion of the spectrum or by thermal collision do not dissociate into atoms except on collision with water molecules. While dissociation does not affect the thermal decomposition of hydrogen iodide, the thermal and photochemical union of hydrogen and bromine and the thermal combination of hydrogen with iodine can be stopped by desiccation.

In the combination of hydrogen and bromine the commencement of the chain mechanism, so marked in the hydrogen-chlorine reaction, can be detected at high temperatures and high pressures of hydrogen. The relationship between the mean life of the excited bromine molecule and the water-vapor pressure required for the attainment of a velocity maximum of combination is developed. With a value of $\tau = 10^{-7}$ sec., this pressure is found to be of the order of 0.1 mm. A mechanism for the combination of hydrogen with iodine based upon the primary dissociation of iodine into atoms is advanced and this system is shown to be photochemically sensitive at high temperatures (450°) in accordance with theoretical considerations. It is considered unnecessary to assume that the chain mechanism involves water.

CAMBRIDGE, ENGLAND

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

THE FREE ENERGY OF FORMATION OF ZINC OXIDE[1]

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This article is the last of three dealing with the free energy of formation of zinc oxide. Four possible methods of experimentally determining the standard free energy of stable oxides usually are available: (1) measurement of high-temperature equilibria and extrapolation of the results; (2) measurements dependent on the electromotive force of reversible galvanic cells; (3) calculation from low-temperature specific-heat data and the third law of thermodynamics; (4) calculation from solubility values and standard electrode potentials. The present work reports new experimental results

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chiefly from the second and third methods, but offers comparative values from all four methods.

Aside from the utilitarian value of accurate data of this sort, the results may have some general theoretical interest in that they constitute, as far as is known, the first case in which these four methods have been investigated on the same substance sufficiently to enable some comparison to be made.

In the first paper, Maier[5] recalculated the existent vapor-pressure data of zinc to render them consistent for thermodynamic calculations, and in the second Maier and Ralston[6] presented results of equilibrium experiments on the reduction of zinc oxide by carbon monoxide, from which the free energy of formation was first calculated. Certain peculiarities of the high-temperature reduction work made desirable further confirmation of the results obtained. The first part of the present work, performed by Maier at the Pacific Experiment Station of the Bureau of Mines, at Berkeley, deals with cell measurements involving zinc oxide electrodes. Parks then became interested in the problem, and determined low-temperature specific-heat values with the assistance of Mr. C. T. Anderson, in the Chemical Laboratory of Stanford University.

I. The Zinc Oxide Electrode

The possibility of setting up a reversible zinc oxide electrode would seem to depend upon the failure of dilute alkaline solutions in contact with zinc oxide to give true solutions of zincate, and upon the metastability of zinc hydroxide at ordinary temperatures. If these conditions exist, a cell of the type $H_2(g)$ | dilute alkaline solution | $ZnO(s) + Zn(s)$ should give directly the free-energy change in the reaction $H_2(g) + ZnO(s) = Zn(s) + H_2O(l)$, from which the free energy of formation of zinc oxide is calculable.

The experiments of Hantzsch[7] indicate that a solution of $ZnSO_4 + 9NaOH = Na_2SO_4 + Zn(OH)_2 + 7NaOH$ in 200 liters has almost exactly the same specific conductivity as a solution of $Na_2SO_4 + 7NaOH$ of the same dilution; moreover, the saponification of ethyl acetate at 15° in a solution of $1ZnSO_4 + 12NaOH$ in 100 liters is the same as for $Na_2SO_4 + 10NaOH$ per 100 liters.

The conclusion of Hantzsch that in dilute solutions of zinc hydroxide in alkali, essentially a colloidal form of zinc hydroxide exists, with only small amounts of true zincate, seems justifiable. Barium hydroxide solution, which is more suitable for cells of the type mentioned than solutions of sodium hydroxide, might well be expected to form even lower concentra-

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[5] Maier, This Journal, **48**, 356 (1926).

[6] Maier and Ralston, *ibid.*, **48**, 364 (1926).

[7] Hantzsch, *Z. anorg. Chem.*, **30**, 298 (1902).

tion of true zincate, despite the fact that definite crystals of barium zincate have been prepared from strong solutions by Bertrand.[8]

That crystalline zinc hydroxide, as well as the gelatinous form, is metastable at 30° with respect to zinc oxide was shown by F. Goudriaan.[9]

Experimental Methods

In setting up cells of the type $H_2(g) \mid \text{dil. } Ba(OH)_2 \mid ZnO(s) + Zn(s)$, the form of circulating cell with automatic magnetic pump, as used by Smith and Woods[10] in work on lead monoxide, was duplicated with only minor change of dimensions, and further description will be omitted here. No change in the procedure given there was made, except that in the case of zinc, elaborate precautions for the exclusion of oxygen were not found essential. The auto-oxidation of the metallic zinc in the cell soon robs the solution of traces of dissolved oxygen. The cells were, of course, hermetically sealed against contact with the atmosphere as soon as they had been filled. It was found necessary, however, to boil the solutions of barium hydroxide in contact with c. p. zinc shavings, and out of contact with air before using the solutions in the cell. Even after several recrystallizations of the c. p. barium hydroxide used in making up the solutions, small amounts of metals electronegative to zinc were still present. Since a deposit of only a few molecules' thickness upon a metal is capable of affecting the electromotive force when the metal is used as an electrode, these impurities had to be removed, and this was best done by previous treatment of the solutions with pure zinc.

The thermostats used in controlling the temperatures were constant to about 0.02°, and temperatures read were corrected by a thermometer with Bureau of Standards calibration. In the first work reported, an improvised potentiometer was used, consisting of a Kohlrausch slide wire with appropriate external resistances, and a standard cell with a portable galvanometer sensitive to 0.1 millivolt. This was later replaced by a modern type of potentiometer, and a more sensitive galvanometer, so that readings could be made to 0.01 mv. The earlier potentiometer was compared with the new instrument, but showed no error greater than its limit of reading. The standard cell was also checked against another of a different manufacturer, and showed the represented voltage to within 0.01 mv.

Forms of Zinc and Zinc Oxide

In setting up the zinc oxide electrode, finely divided, c. p., electrolytic zinc was intimately mixed with the various forms of zinc oxide and packed about a platinum electrode that had an electrolytically deposited coating of zinc. The use of amalgam has often been advocated in order to ensure

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[8] Bertrand, *Compt. rend.*, **115**, 939, 1028 (1892).

[9] Goudriaan, *Rec. trav. chim.*, **39**, 505 (1920); *C. A.*, **15**, 479 (1921).

[10] Smith and Woods, This Journal, **45**, 2632 (1923).

that the electrode be in a standard, reproducible state. It was found, however, in work upon the cadmium oxide electrode (to be reported elsewhere) that cadmium amalgam electrodes were *not reversible in basic solutions.* When cadmium amalgam was anodically polarized in a barium hydroxide electrolyte, with a current of only a few micro-amperes, the resulting oxide-hydrate contained both mercuric oxide and cadmium oxide or hydroxide, from which the mercury was not replaced by cadmium after months of standing. In view of this experience, no attempt to use zinc amalgam was made. In any case, Dr. Merle Randall (in a personal communication) has stated that the electromotive force between a deposited zinc electrode and zinc amalgam in zinc salt solutions becomes zero when equilibrium is reached.

For the electrodeposition of zinc upon the electrode, two solutions were used, designated below as basic and acid. The former was a slightly ammoniacal zinc sulfate solution containing ammonium sulfate; the latter was an originally neutral solution of zinc sulfate made slightly acid with acetic acid. Both solutions were permitted to stand in contact with c. p. zinc shavings for several weeks before use, in order to eliminate traces of electronegative metals (especially lead and cadmium) present in the zinc sulfate used. In all later work, when no designation as to the type of deposit is made, that from acid solution is implied. No addition agents were used in either solution, since no difficulty was met in securing dense, and apparently noncrystalline deposits. The anodes of the plating bath were of platinum.

The experiments described here fell chronologically into four groups. In the first and fourth, the zinc oxide used was a commercial c. p. product. Two samples were available, a "dry-process" zinc oxide which had electronegative impurities of 0.005% of lead and a trace of cadmium, and a "wet-process" oxide containing the same amount of lead, but free from cadmium. In Series II, zinc hydroxide was used instead of oxide, because it was feared that local action in the earlier cells might have produced metastable hydroxide, and that the cells previously measured might have involved zinc hydroxide electrodes, instead of zinc oxide. The hydroxide was made by the slow addition of normal, c. p. zinc sulfate solution to normal potassium hydroxide solution free from carbon dioxide until slight turbidity ensued. After the mixture had stood for several weeks during frequent shakings, a good crop of crystalline zinc hydroxide was obtained, which was washed free from sulfate by repeated decantation with water free from carbon dioxide.

In Series III a number of samples of zinc oxide were used which had been subjected to various degrees of heating, both in the presence and absence of zinc vapor. The purpose of these experiments was to ascertain whether any evidence of the formation of solid solutions of zinc in zinc oxide, and *vice versa,* or of allotropic modification of zinc oxide, could be found by cell measurements.

Samples designated as "Blue Powder Nos. 1 to 11" were prepared by sealing an intimate mixture of "dry-process" oxide and C. P., electrolytic zinc shavings into an evacuated (0.01 mm.) silica capsule. The capsule was heated in a tube furnace at the temperatures indicated for a period of not less than 36 hours, and finally quenched practically instantaneously in cold water. In the case of No. 11, a mixture of carbon dioxide snow and alcohol replaced the water. The sample designated as No. 12 was a "blank," in which no zinc had been mixed with the oxide. The sample designated as "recrystallized" was part of a large sample that had been prepared for specific-heat work. It was made by sealing "dry-process" oxide into an evacuated (0.01 mm.) silica flask, and heating to approximately 1100° for about 60 hours. Under these circumstances, considerable shrinkage ensued and the product was microcrystalline under the microscope. The sample designated as C. P. zinc dust was obtained through the courtesy of the New Jersey Zinc Company; it contained metallic zinc, 92.70%; zinc oxide, 7.70%; lead, 0.002%; cadmium, 0.002%; arsenic, 0.0005%.

Measurements of Electromotive Force

Table I shows the early measurements with the less sensitive potentiometer. In all cases each cell represents a filling with new material, and replating of the electrode. In all cells of this series at 25° the electromotive force indicated was reached after a period of approximately 48 hours after immersion in the thermostat, and was constant for periods not less than 48 hours beyond that time; and in some cells constancy was maintained for the period of a week or longer. The cells were not, however, completely permanent, because of the gradual leaching of traces of electronegative impurities from the oxide, and subsequent deposition of the more noble metal upon the zinc. This slow action resulted in ultimate progressive decrease of electromotive force. In the cells at 45° this action was accelerated, and some uncertainty exists in determining the "point of constancy." Moreover, local action at the zinc electrode, with the evolution of some hydrogen, was noticeable at 45°. It is probable that both the drift and local action could have been prevented had oxide of absolute purity been available. To prepare such material seemed hopeless, but an attempt was made at purification by boiling the oxide samples with pure zinc shavings in a barium hydroxide solution. This relieved, but did not cure, the difficulty. These facts, together with the uncertainty as to the heat of formation of zinc oxide discussed in the article by Maier and Ralston mentioned above, emphasized the desirability of more measurements at the elevated temperature. Table IV shows the results of six cells (three sets in duplicate) obtained in later measurements with the more sensitive potentiometer.

In Table II, two values are given for zinc hydroxide cells. These values are not to be considered of the same order of accuracy as those of Table I, inasmuch as the hydroxide cells showed a more or less continual drift, probably due to slow decomposition of the hydroxide form. The "point of constancy" in these cells was uncertain to perhaps slightly more than one millivolt.

The measurements shown in Table III were made under conditions identical with the 25° measurements of Series I, and were of the same accuracy with respect to the "point of constancy."

Table I

Series I; Zinc Oxide Cells, Early Measurements

Cell	Temp., °C. (corr.)	Nature of Zn electrolyte for deposit	Form of ZnO	Moles of $Ba(OH)_2$ per kg. of H_2O	Pressure of H_2 at measurement	E.m.f. obs.	E.m.f. at H_2 = 1 atm.
1	24.83	basic	dry proc.	0.0932	744	−0.4202	−0.4199
2	24.83	basic	dry proc.	.0455	745	− .4201 (5)	− .4199
3	24.83	acid	dry proc.	.0282	746	− .4200	− .4197
4	24.83	acid	dry proc.	.1131	750	− .4201	− .4199
5	24.83	acid	wet proc.	.1213	750	− .4200	− .4198
						Av.	− .4198 ± .0001
6	44.92	acid	dry proc.	.1131	699	− .4286	− .4275
7	44.92	acid	dry proc.	.0565	699	− .4290	− .4279

Table II

Series II; Zinc Hydroxide Cells at 24.83°

Cell	Moles of $Ba(OH)_2$ per kg. of H_2O	Pressure of H_2 at measurement	E.m.f. obs.	E.m.f. at H_2 = 1 atm.
8	0.2262	745	−0.4139	−0.4136
9	.0565	745	− .4143	− .4140
			Av.	− .4138

Table III

Series III; Measurements on Blue Powder and Calcined Oxide at 24.83°, and 0.2426 Mole of $Ba(OH)_2$ per Kg. of H_2O

Cell	Sample used	Temp. of preparation of sample, °C.	Pressure of H_2 at measurement	E.m.f. obs.	E.m.f. at H_2 = 1 atm.
10	Blue powder No. 2	486	742	−0.4190	−0.4187
11	3	662	741	− .4202	− .4198
12	4	729	745	− .4203	− .4200
13	6	473	742	− .4201	− .4199
14	8	557	744	− .4202	− .4199
15	9	745	744	− .4197	− .4194
16	11	990	742	− .4200	− .4197
17	ZnO without Zn No. 12	990	744	− .4200	− .4197
18	Recrystallized	1060	742	− .4205	− .4197
19	C. P. zinc dust	1100	745	− .4203	− .4200
				Av.	− .4197 ± .0002

TABLE IV

SERIES IV; MEASUREMENTS OF ZINC OXIDE CELLS AT 44.88°

Cell	Moles of $Ba(OH)_2$ per kg. of H_2O	Pressure of H_2 at measurement	E.m.f. obs.	E.m.f. at H_2 = 1 atm.
20	0.2030	687	−0.42979	−0.42840
20 dup.	.2030	691	− .42783	− .42653
21	.1354	687	− .42859	− .42720
21 dup.	.1354	691	− .42955	− .42825
22	.1015	694	− .42738	− .42616
22 dup.	.1015	696	− .42734	− .42614
			Av.	− .4271± .0009

Calculations

From the data of the first five cells of Table I, the free energy of the reaction $ZnO(s) + H_2$ (1 atm.) $= H_2O(l) + Zn(s)$ becomes, at 297.9°K., $\Delta F = +19{,}373$ cal., and for the cells of Table III $\Delta F = +19{,}368$. Taking the free energy of liquid water at —56,560, the free energy of formation of ZnO(s) from electrolytic zinc is ΔF_{298} = —75,930, with an apparent accuracy of about ±10 cal.

Calculating ΔH from the integrated Gibbs-Helmholtz equation, $(E_2/T_2)-(E_1/T_1) = (\Delta H/NF)[(1/T_1)-(1/T_2)]$, the value at 45° from Cells 6 and 7 leads to a value of ΔH for the reaction of +13,900 cal., whereas the mean value for the six cells of Series IV gives +14,310, and for Cells 22 and 22 duplicate, which showed the best reproducibility, gives +14,960. These results correspond to a heat of formation for zinc oxide of —82,170, —82,580 and —83,230 cal.

It is apparent that the uncertainty in the cell temperature coefficient is such that a definitive value for the heat of formation cannot be derived from these data; at best, the value from electromotive-force measurements may be assumed to be —82,600 ± 500 cal.

Although the heats of formation thus obtained are disappointing, viewed as a determination of thermal data, the results are useful. In the article by Maier and Ralston[6] the older result of Thomsen (85,430 cal.) was criticized in view of Richards' later determinations of the heat of solution of zinc, and a new heat of formation, —83,097, was calculated, using Roth's figure for the heat of formation of water, —68,280. The value of Lewis[11] for water, —68,330 at 291°K., might have been used with somewhat greater fitness, resulting in a calculated heat of formation of zinc oxide at 291°K. of —83,047 cal. The work on cell temperature coefficients is sufficient to confirm the recalculated amount, as compared to Thomsen's. Moreover, further confirmation has recently become available through the work of Charles E. Hablutzel[12] who, at the suggestion of Dr. Parks, made some

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[11] Lewis, THIS JOURNAL, **28**, 1390 (1906).

[12] Hablutzel, Master's Degree *Thesis*, Stanford University, 1926.

direct determinations of the heat of solution of zinc oxide in acid of the same strength as used by Richards and co-workers. Upon combining the values obtained with Richards' data on the heat of solution of zinc metal, the heat of formation of zinc oxide was found to be —83,423 cal. The direct check thus found is considered somewhat more satisfactory than the indirect calculations of Maier and Ralston. In view of these facts, the heat of formation obtained from the cell coefficient shows rather definitely that the cell reaction occurring actually represented the reduction of zinc oxide.

Had the reaction been $Zn(OH)_2(s) + H_2(g) = Zn(s) + 2H_2O(l)$, it can be shown from thermal data that the heat of this reaction should be about +17,000 cal., rather than the 14,310 actually found for the reaction $ZnO(s) + H_2(g) = Zn(s) + H_2O(l)$. The difference is sufficiently greater than the experimental error to justify further the conclusion that the cell that we measured actually involved the zinc oxide electrode.

Accepting the heat of formation of zinc oxide as —82,600 cal. from cell measurements, and using —75,930 as the free energy at 298°K., the entropy of a formula weight of zinc oxide is calculated as 11.46 cal. per degree. If, however, the recalculated value from thermal data be taken, $\Delta H =$ —83,047 at 291°K., or —83,037 at 298.1°K., S_{298} for ZnO becomes 10.01.

The data on the zinc hydroxide cells cannot be regarded as an entirely satisfactory determination of the free energy of zinc hydroxide, but some tentative calculations may be made. For the reaction $Zn(OH)_2(s) + H_2(g) = Zn(s) + 2H_2O(l)$, $\Delta F_{298} = +19{,}100$. The free energy of formation of zinc hydroxide from its elements then becomes $\Delta F_{298} = -132{,}220$ cal., and for the reaction $ZnO(s) + H_2O(l) = Zn(OH)_2(s)$, $\Delta F_{298} = +240$ cal. The data indicate that zinc hydroxide is actually metastable at 25°, although as far as free-energy data are concerned, the driving force of the reaction must be small. This checks the purely chemical observations of Goudriaan.

II. Heat Capacity of Zinc Oxide at Low Temperatures and the Free Energy from the Third Law

Method and Materials.—The method used was that of Nernst, employing an aneroid calorimeter and measuring "instantaneous" heat capacities. The apparatus and details of experimental procedure are given by Parks and Kelley,[13] and will not be discussed further.

Three samples of zinc oxide were used, designated as Samples 1, 2 and 3.

Sample 1 consisted of large, nearly colorless crystals, obtained through the courtesy of the New Jersey Zinc Company. These crystals are formed during zinc retorting from leaks in a cracked retort. As originally obtained, the crystals varied in color from nearly pure white to buff. The samples used for experimental purposes were hand picked, as nearly colorless as

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[13] Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

possible. The material was the same as that used by Dr. W. P. White, of the Geophysical Laboratory, for high-temperature specific heats, and for which these data are given in the paper of Maier and Ralston. An analysis at Stanford University gave 0.12% of silica, 0.05% of free zinc and a trace of iron. Sulfate, chloride, lead or cadmium, calcium or magnesium could not be found. Some zinc oxide electrodes were set up with this material, but are not described in Part I, as no constant cells resulted. In the cell work, the deposited zinc of the electrode, being dissolved after the cell was dismantled, gave a definite qualitative test for cadmium, so that the analysis above, although adequate for judging the purity for specific-heat purposes, apparently was not sufficiently sensitive for small amounts of impurities. It is estimated that the total impurities in this sample were about 0.2%. Sample 2 was the "recrystallized," dry-process oxide mentioned in Part I, also used in setting up the cell with "recrystallized" oxide in the measurements of Series III. An analysis at Stanford University showed 0.02% of silica; this analysis was made because the material had been recrystallized at high temperatures in a sealed silica container, and it was feared that some contamination might have resulted. The material had small amounts of sulfate, chloride and heavy metals, but total impurities were indicated to be less than 0.1%. Sample 3 was the "dry-process," commercial, C. P. material used in the first cells. X-ray analysis showed the material to be crystalline. The total impurities were less than 0.1%.

The weight of sample used in an actual determination was approximately 116 g. for Sample 1, 57 for Sample 2 and 44 for Sample 3.

Experimental Results

The results shown in the tables for Samples 1, 2 and 3 are expressed in 15° calories, and the weights are reduced to a vacuum basis.

The data here show that all three samples, despite a marked difference in the degree of subdivision of the material, gave the same heat capacities to within the experimental error. At 275°K. (that is, 2°C.) the very fine material, Sample 3, averaged only about 0.25% higher than Samples 1 and 2. This result was somewhat unexpected, inasmuch as Parks and Kelley[13] found that in the case of two samples of ferric oxide, the finer powder averaged about 3% higher than large crystals. Perhaps the larger difference observed by Parks and Kelley in the case of ferric oxide was due to some definite difference in structure and composition of the two samples other than the degree of subdivision.

Calculations

Entropy calculations were made from a smoothed curve, more especially from the data of Samples 1 and 2, individual points showing about 0.1% deviation. Data for Sample 3 would fit this smoothed curve to better than 0.25%.

TABLE V

EXPERIMENTAL RESULTS, HEAT CAPACITY OF ZINC OXIDE; SAMPLE 1

Temp., °K.	C_p per mean g. atom	Temp., °K.	C_p per mean g. atom	Temp., °K.	C_p per mean g. atom
91.3	1.93	109.6	2.34	198.0	3.83
97.5	2.05	152.8	3.11	275.4	4.67
102.9	2.17	160.7	3.24	288.2	4.81
107.7	2.27	193.7	3.75	291.0	4.84
		SAMPLE 2			
88.1	1.86	108.5	2.29	275.3	4.67
93.8	1.99	113.9	2.40	275.3	4.67
97.4	2.06	170.1	3.39	275.5	4.67
99.1	2.09	193.5	3.76	277.2	4.68
102.4	2.18	197.3	3.81	293.8	4.86
104.6	2.21	203.0	3.88	294.8	4.85
108.2	2.28	207.3	3.97		
		SAMPLE 3			
99.0	2.08	195.4	3.76	275.3	4.68
104.7	2.22	198.6	3.82	275.8	4.69
108.2	2.28	201.8	3.89	288.0	4.81
109.5	2.31	205.0	3.93	288.8	4.82
113.0	2.37	274.9	4.67	289.0	4.83
114.1	2.39	274.9	4.69		

From 0°K. to 88°K., the entropy as calculated by the "n formula" of Lewis and Gibson ($n = 0.67$) is 2.3 entropy units. From 88°K. to 298.1°K., the entropy obtained by graphical summation is 8.05 units, and $S_{298} = 10.4$ cal. per degree.

The data on zinc oxide lie considerably above the "standard" heat-capacity curve at low temperatures and the large proportion of the entropy at 298°K. which has to be calculated from the "n formula" causes a somewhat higher uncertainty in the entropy than usual. The experimental work should be extended to liquid hydrogen temperatures to ensure a truly good value.

Accepting the recalculated thermal value for the heat of formation of zinc oxide as —83,037 cal. at 298°K., the free energy is calculated from the experimental value of the entropy to be —76,037 cal.

III. Calculation of Free Energy from Solubility Measurements

Omitting the earlier determinations of Bodländer[14] who deduced the solubility of zinc hydroxide from electromotive-force measurements, the available data on solubility are comprised in the work of Herz,[15] who determined the distribution of acid radicals (sulfate, nitrate and chloride) between zinc hydroxide and ammonia; the work of Dupré, Jr., and Bialas[16] who made the only direct determinations of the solubility of zinc oxide by

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[14] Bodländer, *Z. physik. Chem.*, **27**, 66 (1898).

[15] Herz, *Z. anorg. Chem.*, **23**, 227 (1900).

[16] Dupré and Bialas, *Z. angew. Chem.*, **16**, 55 (1903).

conductivity and analytical methods; and the recent work of Miss de Wijs,[17] who calculated the solubility of zinc hydroxide from measurements of the partial pressure of ammonia over zinc-ammonium complex ions.

The first experiments of Herz were made with ammonium salt concentrations near quarter molal. The reaction occurring was supposedly $Zn(OH)_2(s) + 2NH_4Cl \rightleftharpoons ZnCl_2 + 2NH_3.H_2O$, but the corresponding formal equilibrium constant for the reaction, as calculated from the experimental data, did not show even approximate constancy, and this was apparently caused by the formation of complex ammonium ion. Later experiments with more dilute solutions showed an apparent constancy over a small range of concentrations, leading to a value of the solubility of 1.3×10^{-5} moles per liter at 18°. Herz did not correct for the activity of the various ions entering the reaction, because of the uncertainty of the experimental values. We have made such corrections, using the principle of ionic strength of Lewis and Randall, but find that no appreciable change is produced in the calculated solubility by this correction. From the solubility product of zinc hydroxide thus obtained and from the reaction $ZnO + H_2O = Zn^{++} + 2OH^-$, using the free energies of the zinc and hydroxyl ions at 25° given by Lewis and Randall, without correction to the basis of 18° at which the solubility measurement was made, the free energy of zinc oxide is calculated from Herz's work to be $\Delta F_{298} = -72{,}500$ cal.

Dupré and Bialas give the solubility of zinc oxide determined by conductivity as 1 part in 236,000 of water, but by analysis of a saturated solution, with precipitation of the zinc as sulfide, 1 part in 217,000 of water. No details of the work with zinc are given in the original communication, and it may be doubted whether sufficient precautions were taken to eliminate the traces of soluble impurities that usually are present in zinc oxide; we shall take the lower value as probably better. This value corresponds to a molal solubility of 5.2×10^{-5}, from which the free energy of zinc oxide is calculated as $\Delta F_{298} = -70{,}400$ cal.

The work of Miss de Wijs seems to have adequately solved the difficulty in Herz's experiments, permitting the effect of the zinc-ammonium complex ion to be evaluated. The solubility product given in her work is 7.4×10^{-17}, leading directly to the value $\Delta F_{298} = -75{,}380$ for the free energy of formation of zinc oxide.

IV. Comparison of Results of Different Methods and General Conclusions

In Table VI are summarized the experimental and derived values of heat of formation, free energy and entropy as obtained by the various methods. The results obtained directly are shown in ordinary type, and the calculated or derived values in italics.

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[17] de Wijs, *Rec. trav. chim.*, **44,** 663 (1925).

Before comparing the results obtained by high-temperature equilibria, and those dependent on cell measurements, the question of allotropic modifications of zinc must be considered. References are found in the literature to at least three supposed transition points for zinc, but the data are conflicting. Despite the apparent confirmation of at least one of these points from the work of Miss Bingham,[18] and from the more recent experiments of Stockdale,[19] the specific-heat work of Eastman, Williams and Young,[20] and of Behrens and Drucker[21] failed to indicate any anomalies in the temperature range in which the transitions were supposed to exist. Although it must be admitted that the experiments of Miss Bingham and of Stockdale would seem to show that the transitions had a time lag, making their disclosure from specific-heat measurements difficult, the latter determinations justify belief that the energy change, if it exists, must be small. Although the point is still somewhat uncertain, we shall assume that the electrodeposited zinc is in the same state as that existing at high temperatures, and that the results of the table are strictly comparable.[22]

TABLE VI

COMPARISON OF VALUES FOR ZINC OXIDE AT 25°

Method	Heat of formation, cal. per mole	Free energy of formation, cal. per mole	Entropy at 298°K., cal. per degree per mole
Thermal data	−83,037[a]		
	−82,970[b]		
	−83,000[c]		
	−83,423[d]		
Equilibria[e]			
$ZnO + CO = Zn + CO_2$	−82,830	−75,785	*10.20*
E.m.f.			
$ZnO + Zn \mid Ba(OH)_2 \mid H_2$	−82,600 ± 500	−75,930	*10.01*[f]
Specific heats and third law		*−76,037*	10.4
Solubility determinations		−75,380	
"Best values"	−83,000	−75,930	10.20

[a] Based on the work of Richards, Rowe and Burgess. [THIS JOURNAL, **32**, 1176 (1910).] See also Ref. 6.

[b] De Forcrand, *Ann. chim. phys.*, [7] **27**, 36 (1902), ZnO from $Zn(OH)_2$.

[c] De Forcrand [Ref. b], ZnO from $Zn(NO_3)_2$.

[d] From a graduate thesis at Stanford University, Charles E. Hablutzel, "The Heat of Formation of Zinc Oxide," **1925**.

[e] See Ref. 6, also, for discussion of Refs. *a*, *b* and *c*, above.

[f] Calculation from thermal values of ΔH.

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[18] Bingham, *Nat. Phys. Lab. J. Inst. Metals*, **24**, 323 (1920).

[19] Stockdale, *J. Chem. Soc.*, **127**, 2951 (1925).

[20] Eastman, Williams and Young, THIS JOURNAL, **46**, 1178 (1924).

[21] Behrens and Drucker, *Z. physik. Chem.*, **113**, 79 (1924).

[22] Since this was written, Scientific Paper No. 522, of the United States Bureau of Standards, has appeared: "Pure Zinc at Normal and Elevated Temperatures," by Freemann, Sellers and Brandt, offering definite data to indicate that no allotropy exists.

In the values of the table, the calorimetric thermal data seem to us best for the heat of formation, and the final value is considered to be $\Delta H_{298} =$ —83,000 ± 300 cal. per mole.

In the case of the free-energy results, the value from electromotive-force measurements, which should be the most accurate, is nearly exactly the mean of that obtained from equilibria, and from the third law, and the best figure may be taken as $\Delta F_{298\cdot1} =$ —75,930 ± 150 cal. per mole.

For the entropy, the value derived from equilibria, which is again the mean of that from specific heats, and from electromotive-force measurements, is probably the "best" acceptable result until such time as the specific-heat data have been extended to lower temperatures. Then for zinc oxide $S_{298} = 10.2 \pm 0.2$ cal. per degree.

The deviations given above are maximum deviations, and not the average deviation from the mean, which latter would be considerably less in case only the more accurate data are considered.

Aside from the numerical implications of the data presented, a further general conclusion may be drawn from this work which is of interest and importance, especially to metallurgists. There is no evidence that "chemical blue powder," if by this term solid solutions of zinc in zinc oxide or *vice versa* are understood, or the allotropic modifications of zinc oxide postulated by De Forcrand, exist.

Summary

Final numerical values for the heat of formation, free energy of formation, and entropy of zinc oxide are deduced from four entirely independent experimental methods.

For zinc oxide reduction, equilibria at high temperatures furnish the most satisfactory determinations of thermodynamic constants.

The electromotive-force method seemed to furnish the most accurate free-energy determination, but involved difficulties in the determination of heats of formation in the case of zinc oxide.

Results for zinc oxide derived from the third law are satisfactory for practical purposes, but have not been carried to sufficiently low temperatures to furnish a complete test of the third law on this material.

Values of free energy obtained from solubility determinations were the least satisfactory, but were moderately concordant when good solubility data were available.

No evidence of allotropic modification of zinc or zinc oxide, with energy amounts greater than 300 calories, could be found, and solutions of zinc in zinc oxide or *vice versa*, do not exist, to a degree discernible by the methods used.

A preliminary value of the free energy of zinc hydroxide has been obtained.

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