Summary

Pure acetophenone, contrary to the findings of Nicollier, is decomposed by light.

The reaction of sodium iodide on acetophenone is certainly not a simple reversible photochemical reaction.

The quantity of iodine liberated in such a solution is independent of the concentration of sodium iodide present, and apparently depends only upon the time and the intensity of the light and, consequently, upon the quantity of acetophenone decomposed.

The presence of water hastens the formation and increases the quantity of the flaky, white precipitate produced by light in acetophenone-sodium iodide solutions.

The tentative explanation offered for the photochemical reaction studied is that an acidic substance, such as benzoic acid, formed from acetophenone by the light, reacts with the sodium iodide—a thermal reaction—producing hydriodic acid and a precipitate of sodium benzoate, the hydriodic acid being further oxidized by the light into free iodine and water.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SPECIFIC HEATS OF MAGNESIUM, CALCIUM, ZINC, ALUMINUM AND SILVER AT HIGH TEMPERATURES

BY E. D. EASTMAN, A. M. WILLIAMS AND T. F. YOUNG

RECEIVED MARCH 4, 1924

In previous papers from this Laboratory[1,2] accounts have been given of a study of the connection between the high specific heats and the electropositive character of certain metals. The present experiments were undertaken in order to extend this study to other metals and to higher temperatures. This paper will be confined to a description of the measurements and record of the results; the theoretical aspects will be discussed in the paper immediately following this.

The Experimental Measurements

The method adopted in this work for the specific-heat measurements is the ordinary one,[3] in which a known mass of the desired substance at a known temperature is transferred to a calorimeter at a lower temperature, and the temperature rise in the latter noted, the heat capacity of the calorimeter being independently determined.

The heating of the metal was carried out in a tube resistance furnace, the working chamber of which was 20 cm. long and 3 cm. in diameter.

[1] Lewis, Eastman and Rodebush, *Proc. Nat. Acad. Sci.*, **4**, 25 (1918).

[2] Eastman and Rodebush, THIS JOURNAL, **40**, 489 (1918).

[3] The method has been discussed at length by White, *Am. J. Sci.*, [4] **47,** 1 (1919).

At each end of the furnace three closely fitting Transite board partitions with air spaces between them were provided, reducing the effective working chamber to a length of 10 cm. At the center of this space a block of the metal, which had been sealed in a vacuum in a platinum can, was suspended by a fine Nichrome wire.

The temperature in the interior of the metal was measured by means of a platinum and platinum-rhodium thermocouple, the end of which fitted into a small tube extending to the center of the can.

The thermocouple was calibrated and repeatedly checked at several fixed points which included the melting and boiling points of water, the melting points of samples of tin and zinc supplied by the Bureau of Standards, and of silver, prepared by the fusion of purified silver chloride and sodium carbonate. In order further to define the calibration curve in the region between the melting points of zinc and silver, a comparison was made at 630° with a platinum resistance thermometer which had been standardized at the fixed points mentioned above, silver excepted. The readings of the thermocouple were interpreted with the aid of the standard curve of Adams.[4] The potentiometers which were used permitted temperatures to be read to 0.1°. The error probably did not exceed 1°.

At 500° the maximum temperature difference in the empty furnace between center and the positions of the ends of the can was 5°. The difference between the average temperature of the block of metal, and that recorded by the thermocouple at its center could not well have exceeded 2.5° at this temperature, and since the metals are far better thermal conductors than air, the difference was probably not more than 1°.

The metal was transferred from the furnace to the calorimeter only after the furnace temperature had been held constant for at least 15 minutes. The transfer was accomplished by swinging the furnace, which was supported on a movable frame, into position over the calorimeter and releasing the can by electrically fusing the Nichrome supporting wire. The Transite partitions at the bottom of the furnace were automatically removed during the swing. Immediately after the transfer, the furnace was swung back. The cover of the calorimeter and a metallic shield used to protect it from radiation from the furnace during heating were then replaced. The entire operation of dropping required but a few seconds. Doubling or tripling the normal time of approach and release caused no noticeable changes in the results.

The calorimeter consisted of a copper can of 2 liters' capacity, polished on the outside and suspended inside a larger brass can, which was itself polished inside and completely jacketed with silk floss. The distance between the calorimeter and the walls of the outer can was about 4 cm.

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[4] Adams, THIS JOURNAL, **36**, 65 (1914).

Between the walls two equally spaced reflecting cylinders of the copper were suspended. The neck of the calorimeter, by which it was supported from the top of the outer can, and through which the sample dropped, was made of very thin nickel silver, as were also the two smaller tubes which served to admit a stirrer and thermometer. Six wires attached to the inside walls served as a basket to catch the charge of metal, to hold it at the center of the calorimeter. The stirrer was of glass, of the twisted strip type, and was rotated at a constant rate fast enough to produce thorough mixing of the water, but without appreciable heating effects.

Temperatures in the calorimeter were measured with a resistance thermometer[5] and bridge of the Bureau of Standards design. The readings of the thermometer were interpreted by a quadratic equation, the three constants of which were determined from the resistance at the ice and steam points and at the transition point (32.383°) of sodium sulfate. The sodium sulfate had been recrystallized until no further effect upon its transition point was produced. The temperature rises in the calorimeter were corrected for loss of heat during the period of interchange by extrapolation of time temperature curves to the time of dropping the metal into the calorimeter. In from 10 to 20 minutes after the drop nearly every curve was sufficiently well defined to be extrapolated with an uncertainty of not exceeding 0.001 or 0.002°. The extrapolation was over a range usually less than 0.02°, but in a few instances as great as 0.03° to 0.05°.

The heat capacity of the calorimeter was determined by noting the temperature rise when a measured quantity of heat was developed electrically within it. The heating interval was about 10 minutes and the error due to correction for heat losses was estimated as not exceeding 0.15%. The combined error of the electrical and time measurements was of the order of 0.1%.

The heat capacity of the platinum container and heat losses from the charge during its drop were corrected for by measuring the temperature rises when the empty container at various high temperatures was dropped into the calorimeter. These corrections varied from 2.5% of the total effect in the case of aluminum to 6% in the case of silver.

The amounts of the metals used in moles were approximately as follows: magnesium, 1.35; calcium, 1.13; aluminum, 2.77; zinc, 1.85; silver, 1.02.

The magnesium was a commercial product, cast in sticks. Qualitative tests for aluminum, iron and silica showed that it contained only negligible amounts of these impurities. Analysis of the calcium showed 97.75% of the element, 0.85% of chlorine, and 1.08% of iron and aluminum as oxides. The aluminum was obtained from the

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[5] In the work on magnesium, calorimeter temperatures were measured with a 20-junction thermoelement, which was later calibrated by reference to the resistance thermometer. With it readings could be made to 0.0001°.

Bureau of Standards. As it was intended to be used as a standard in thermometry it was presumably quite pure. The zinc was a pure commercial product; tests revealed only negligible quantities of lead, cadmium and iron. The silver was the melting-point sample previously described.

The Experimental Results

The direct results obtained from the measurements were "total heats" of the metals between 20° and a series of temperatures from 100° up. These total heats were expressed by equations of the form

$$h = a + bt + ct^2 \qquad (1)$$

where h represents the heat, in calories per mole, evolved on cooling the metal from t to 20°, and a, b and c are constants determined from the data. The residuals (h exptl. − h calcd.) were seldom more than 0.5% of the total at any temperature and usually much less. Table I summarizes the facts concerning the various determinations.

TABLE I

DATA CONCERNING "TOTAL HEAT" DETERMINATIONS

Metal	a	b	$c \times 10^3$	Temp. range °C.	Temp. int. °C.	No. of drops	Av. residual %
Mg	−120.5	5.998	1.306	100 to 615	27	20	0.31
Ca_α	−124.0	6.091	2.086	100 " 400±	37	8	.35
Ca_β	− 17.5	6.610	0.7608	400 " 605	50	4	.35
Al	−132.2	5.901	1.306	100 " 590	45	12	.20
Zn	−110.0	5.908	1.518	100 " 405	23	14	.37
Ag	−138.5	6.02	0.76	100 " 900	73	12	.31

Cols. 2, 3 and 4 of Table I give the constants of Equation 1, Col. 5 the temperature range in which the equation is applicable, Col. 6 the average temperature interval between drops, Col. 7 the number of runs, and the last column the average percentage deviation of all the individual experiments from the value calculated from the equations.

A transition point in calcium at about 400° was revealed by a break in the total-heat curve at this temperature. A repetition of the measurements (with a different sample of calcium) and several differential cooling curves confirmed this. From the total-heat curve above and below this break the heat of transition was estimated to be 100 ± 25 cal. per mole. The two forms are designated α and β in Table I. The existence of two forms of calcium has not previously been reported. Swisher[6] has studied the variation in resistance of calcium with temperature. While he draws a smooth curve to represent his results, there is indication of a discontinuity, and it appears to us that his data could be better represented by separate curves above and below 400°.

Various observers have reported transition points in zinc. The data, summarized by Wüst,[7] leave considerable doubt as to whether more than

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[6] Swisher, *Phys. Rev.*, [2] **10**, 601 (1917).

[7] Wüst, *Ver. deutsch. Ing. Forschungsarb.*, No. 204 (1918).

one form exists. No evidence of a transition was found in our calorimetric work. Differential cooling curves made with copper as a reference substance, and using copper-constantan thermocouples in conjunction with a sensitive potentiometer to measure temperatures, also failed to reveal any transition point in the range of our measurements. It is our opinion that there is no transition in this region.

The atomic heat capacity at constant pressure, C_p, is readily obtained at any temperature included in Table I from the values of the constants given there, by means of the equation,

$$C_p = \mathrm{d}h/\mathrm{d}t = b + 2ct \tag{2}$$

The values of C_p so obtained are tabulated at 100° intervals in Table II.

TABLE II

ATOMIC HEAT CAPACITIES, IN CALORIES PER DEGREE, OF METALS AT VARIOUS TEMPERATURES

Temp. °C.	Mg	Caα	Caβ	Al	Zn	Ag
100	6.26	6.51	..	6.16	6.21	6.17
200	6.52	6.93	..	6.42	6.52	6.32
300	6.78	7.34	..	6.68	6.82	6.48
400	7.04	7.76	7.22	6.95	7.12	6.63
500	7.30	..	7.32	7.21	..	6.78
600	7.57	..	7.52	7.47	..	6.93
700	..	..	..	..	..	7.08
800	..	..	..	..	..	7.24
900	..	..	..	..	..	7.39

The specific-heat–temperature curve determined above for magnesium fits well with the curve determined at lower temperatures by Eastman and Rodebush.[2] This is not true of the calcium curve. The present results are some 10% below the previous ones. As the results of Günther[8] indicate a similar discrepancy at low temperatures it is probable that some unsuspected error was present in the former work, although it is possible that it was the beta form of calcium which was then measured. The third law of thermodynamics requires that the curve for β-calcium cross that for α at some temperature below the transition point, and extrapolation of the β curve would come much nearer joining the Eastman-Rodebush curve than that of the alpha form does. For aluminum the present results at the lower temperatures are in excellent agreement with those of Griffiths and Griffiths,[9] Nernst and Lindemann,[10] Wüst,[7] and Schübel.[11] At the highest temperatures reached, our results are 2% greater than Wüst's, and 4% greater than Schübel's. The agreement with the work of the same ob-

[8] Günther, *Ann. Physik*, [4] **63,** 476 (1920).

[9] Griffiths and Griffiths, *Trans. Roy. Soc. London,* **214A,** 319 (1914).

[10] Nernst and Lindemann, *Z. Elektrochem.*, **17,** 817 (1911).

[11] Schübel, *Z. anorg. Chem.*, **87,** 81 (1914).

servers in the case of zinc is again good at low temperatures. In the upper range our curve lies between the very discordant ones of Wüst and Schübel. Our results for silver are in agreement with the others at all temperatures, with the exception of Schübel's curve, which is lower by 2.5% at 500° and higher by the same amount at 900°.

The accuracy of such determinations as these is very difficult to estimate. Recalling that the furnace temperature measurements were probably accurate to within 1° at 500°, that the increases in calorimeter temperature, about 2° or greater when the metal was dropped from the furnace at 500°, were known to within 0.001°, and that the heat capacity of the calorimeter was probably accurate to within 0.25%, the error of measurement may be conservatively estimated as not exceeding 0.5%. The equations used to represent total heats, which may introduce errors in the true specific heats at certain temperatures if the functions chosen are not well suited to the actual variations, were in these cases apparently quite satisfactory. From a study of the residual curves corresponding to them, it appears unlikely that errors in C_p occur which are much larger than the errors of measurement. The largest errors due to impurities in the metals are probably those in the results for calcium, and these are again estimated not greatly to exceed the other errors. On the whole, we believe 1% to be a conservative estimate of the error in the specific-heat values. For calcium it may exceed this slightly; for the other metals it may be appreciably less.

Summary

Measurements of the specific heats of magnesium, calcium, zinc, aluminum and silver in the temperature intervals between 100° and the melting points of the metals are described. The results obtained are estimated to be accurate to within about 1%.

A transition point in calcium has been found at about 400°. No evidence of transition points which have been reported in the literature for zinc could be detected, either in the specific-heat work or by cooling curves.

BERKELEY, CALIFORNIA