[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND THE UNIVERSITY OF ILLINOIS]

THE ATOMIC HEATS OF CADMIUM AND TIN AT LOW TEMPERATURES

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No determinations of the true specific heat of metallic cadmium below 100° K. are to be found in the literature, although Dewar[2] measured the mean specific heat of the metal between the boiling points of hydrogen and nitrogen. Since cadmium offers a possibility of checking the generalization of Sackur, Tetrode, and others[3] in regard to the entropy of monatomic gases, the specific heats of the metal have been measured between 70° K. and 100° K. For substances whose atomic heats at constant volume fall on the characteristic curve found for the metals by Lewis and Gibson,[4] the data over this range of temperature enable one to extrapolate in either direction and obtain the whole specific curve from 0° to 298° K. with almost as great accuracy as it can be readily measured. According to Cohen,[5] cadmium exists in at least 2 allotropic forms with a considerable heat of transformation and consequent difference in entropy. The question was raised as to whether in such a case the atomic heats of the form having the higher entropy and presumably an abnormally high atomic heat at 298° K. would fall on the curve of Lewis and Gibson. In the more familiar case of gray and white tin, Brönsted[6] has measured the specific heats of the 2 forms at liquid-air temperatures but his data do not cover a great enough temperature range to settle the question. Since there is considerable uncertainty about the different modifications of cadmium, it was thought that the question could be most easily settled by repeating Brönsted's measurements on white tin.

Experimental Part

The method used was similar to that used by Eastman and Rodebush[7] except that the apparatus was constructed of metal.

The calorimeter consisted of a brass can of 6 cm. internal diameter and 15 cm. length, with a lid which could be soldered into place in order to make it vacuum tight. A german silver tube 0.5 cm. in diameter and 60 cm. long soldered into a hole in the cen-

[1] This work was done originally while the author was Fellow of the National Research Council at the University of California. Because of uncertainty in the temperature measurements made at that time, the work has since been repeated.

[2] Dewar, *Proc. Roy. Soc. London*, **89A**, 158 (1913).

[3] For references see Tolman, THIS JOURNAL, **42**, 1185 (1920).

[4] Lewis and Gibson, *ibid.*, **39**, 2560 (1917).

[5] Cohen and Helderman, *Verslag. Akad. Wetenschappen Amsterdam*, **23**, 1015 (1914).

[6] Brönsted, *Z. physik. Chem.*, **88**, 479 (1914).

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

ter of the lid served to connect the calorimeter to the vacuum pump and as a means of support, the calorimeter being suspended in a large Dewar tube. The wires for the electrical connections were brought out through this tube which was attached to a Pyrex glass tube at its upper end by de Khotinsky cement. The wires were brought out of the glass tube through a side arm which was closed with cement. Inside the brass can an adiabatic shield of copper was mounted on german silver legs. This shield was wound with a heating coil and provided with a thermocouple and covered inside and out with silver foil to prevent radiation. Inside the shield was hung by a silk thread the block of metal whose specific heat was to be determined. The metal was in the form of a round stick 2 cm. in diameter and 8 cm. long, with a thread of 5 turns to the centimeter cut in its surface, in which the heating coil was wound. An alcoholic solution of shellac applied in the grooves of the heating wire and dried at room temperature was found to make much better thermal contact with the metal at low temperatures than either bakelite or paraffin. The thermocouple was soldered to the metal and the whole was wrapped in silver foil. The use of german silver connections to avoid heat conduction and silver foil to avoid heat radiation proved to be highly satisfactory.

The heating wire was B. and S. No. 36 silk-insulated Therlo and had a resistance of 60 to 70 ohms. The thermocouple was B. and S. No. 36 Ideal wire. The copper connections were all B. and S. No. 35 silk-insulated. It was found absolutely essential to have all the wires attached to the block of metal in good thermal contact with the adiabatic shield, although electrically insulated from it, in order that the heat conducted down the wires might be absorbed by the shield and not reach the metal.

An Edison battery was used as a source of current, the energy input being measured with an accuracy of 0.1% by a voltmeter, ammeter and stop watch, all of which were calibrated. The temperatures were read on a White potentiometer installed in a constant-temperature booth. Temperatures could be read with a precision of 0.002°. The vacuum was maintained by a mercury-vapor pump. A pressure below 0.00001 mm. could be obtained, usually within a few minutes after the pump was started.

The lowest temperatures were reached by evaporating liquid air under reduced pressure.

The thermocouples were calibrated against a platinum resistance thermometer which, in turn, was calibrated against an oxygen vapor-pressure thermometer by the method of von Siemens.[8] The platinum resistance thermometer is not a practical instrument for use at low temperatures on account of variable resistance, but when well seasoned and carefully handled it affords a very satisfactory and accurate means of calibrating a thermocouple. The deviation from the table given by Adams[9] of the observed readings in microvolts for the thermocouple wire used, when plotted against observed readings, gave a very smooth curve. The calibration is believed to be as accurate as the vapor-pressure measurements of oxygen which were obtained by Henning.[10] The values for dE/dT at any temperature were obtained by differentiating the equation of Adams and adding to it the slope of the deviation curve. The wire used was found to be entirely free from inhomogeneities, different pieces of wire checking with each other to 1 part in 10,000. The tin used was an imported grade of good quality and the cadmium was an "analyzed" sample which showed a very high purity. The sample of metal was prepared for the specific-heat determination by fusion in an atmosphere of hydrogen, and maintainance of the temperature near the melting point until the solid phase stable at the melting point had time to form, then cooling the metal rapidly to room temperature.

[8] von Siemens, *Ann. Physik*, [4] **42**, 871 (1913).

[9] "Pyrometry," *Am. Inst. Min. Metallurg. Engineers*, New York, **1920**, p. 170.

[10] Henning, *Ber.*, **44**, 1128 (1921).

Specific-heat Measurements.—The mode of operation was as follows. The block of metal and adiabatic shield were brought to the same temperature, and then heated at as nearly an equal rate as possible for 5 minutes and the energy input recorded together with the temperature. To obtain the rise in temperature, the rise in microvolts was divided by the value of dE/dT for the temperature half way between the initial and final temperatures. The average temperature rise was about 2.5°.

At low temperature there was no appreciable heat interchange between the metal block and the shield for 1° difference in temperature, and in the actual runs the temperature differences were not over 0.1°. As the metal block came to constant temperature within 1 minute after heating, no correction had to be applied for heating or cooling. The heat leak between the shield and outside of the calorimeter was quite small so that the shield could be held at any temperature without difficulty. At 25° C. the heat interchange between metal block and shield was no longer negligible, and here while the runs were made the two were kept at as nearly the same temperature as possible, in the expectation that the errors would be as often positive as negative. Since at higher temperatures it is not possible to keep the shield at a uniform temperature, it would be impossible to make any reliable correction for heat interchange.

The results are given in Table I. The specific heat of the shellac, silk insulation, etc., was estimated at 0.45 cal. per g. at 25° C. and 0.225 at liquid-air temperature. The specific heat of the silver foil, heating wire,

TABLE I

ATOMIC HEATS

CADMIUM

Weights: cadmium metal, 196.70 g., silver foil, 1.84 g.; wire, 0.60 g.; organic matter, 0.22 g.

Temp. °K.	C_p	Temp. °K.	C_p	Temp. °K.	C_p	Temp. °K.	C_p
69.66	4.67	*80.00*	*4.94*	89.91	5.15	99.37	5.31
70.00[a]	*4.68*	80.09	4.96	*90.00*	*5.15*	*100.00*	*5.32*
72.40	4.74	82.59	4.98	92.39	5.21		6.27
							6.31
74.97	4.81	85.06	5.04	94.70	5.23	298	6.20
							6.23
77.56	4.88	87.70	5.11	97.08	5.26	Av.	6.25

TIN

Weights: tin metal, 188.12 g.; silver foil, 1.68 g.; wire, 0.62 g.; organic matter, 0.30 g.

69.63	4.57	*80.00*	*4.87*	*90.00*	*5.11*	*100.00*	5.32
70.00	*4.59*	80.34	4.88	91.26	5.15	101.00	5.34
72.39	4.64	84.00	4.98	93.56	5.17		6.51
75.11	4.74	86.36	5.01	96.21	5.26	298	6.51
							6.49
77.71	4.83	88.90	5.07	98.59	5.27	Av.	6.50

[a] Interpolated data are in italics.

etc., was easily calculated from the existing data. The total of these corrections was 1–2% of the heat capacity of the metal itself.

If the data at low temperatures are plotted, a smooth curve can be drawn through the points with a maximum deviation of 0.4%. Since there are several sources of possible error of the magnitude of 0.1%, the actual error is probably greater than this. The principal source of error in most of the specific-heat data that have been published hitherto, has been the temperature measurements. The errors in absolute temperatures are not serious, but the values of dE/dT for a thermocouple must be obtained from a curve analytically or graphically, and are difficult to obtain with high accuracy. Resistance thermometers, as before noted, are not particularly practical for specific-heat measurements, since they are subject to changes in resistance due to expansion and contraction. It is believed that the calibration of the thermocouple wire used in this work is sufficiently good to give the values of dE/dT with an accuracy of 0.1–0.2%.

The specific heats were measured at 298° K. as a check rather than to obtain new values, since this method is not particularly adapted to working at room temperatures. The value for cadmium agrees well with previous data. The value for tin is somewhat high as compared with the value of 6.47 for C_p at 298° K. obtained by Schimpf.[11] Judging from these results, an accuracy of 1% might be expected with this apparatus at room temperature.

The results at low temperatures, when plotted against the logarithm of the absolute temperature, may be brought into exact coincidence with the characteristic curve for the metals obtained by Lewis and Gibson,[4] except for a slight deviation near 100° K. due to the difference between C_p and C_v. Log. Θ, where Θ is the "characteristic temperature" when $C_v = 3$, is 1.605 for cadmium and 1.625 for tin. These results tend to confirm the accuracy of the original work of Dewar and hence the original entropy calculation of Lewis and Gibson.[4]

The values for tin are higher than those obtained by Brönsted.[6] The explanation for this is to be found, it is believed, in the fact that Brönsted worked with the finely divided metal in a container. At low temperatures thermal equilibrium is difficult to obtain under such circumstances. A solid block of highly conducting metal should give more accurate results.

Summary

The atomic heats of cadmium and tin have been measured between 70° and 100° K. with sufficient accuracy to fix the curves for the metals over the temperature range from 0° to 298° K.

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[11] Schimpf, *Z. physik. Chem.*, **71**, 120 (1910).