

presence of side reactions: pentaphenylcyclopentadienyl, tri-*p*-anisylmethyl and the nitrogen free radical α, α -diphenyl- β -trinitrophenylhydrazyl.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

THE HEAT CAPACITY OF SELENIUM FROM 100 TO 300°A.¹

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RECEIVED MAY 16, 1932

PUBLISHED AUGUST 5, 1932

Previous work on the heat capacity of metallic selenium has been of a rather uncertain nature. None of the experimenters has stated the method of purification so as to have selenium free from tellurium, nor have they shown that their specimens were the metal and not some other form of selenium.

Some of the earliest work was done by Regnault.² He obtained the value 6.63 calories per mole at 98° and 5.93 at 20 to 98°. Bettendorf and Wüllner³ found 6.65 from 25 to 60°. Dewar⁴ gave the value 2.86 between liquid nitrogen and liquid hydrogen temperatures. In our investigation the selenium was carefully purified and annealed to the metallic form. The Nernst method was used to find the heat capacity.

Purification and Preparation of the Sample

A Mallinckrodt grade of selenium was dissolved in concentrated nitric acid. The selenium dioxide was then dissolved in dilute hydrochloric acid. The insoluble material was filtered out and the selenium precipitated with sulfur dioxide. The selenium came down in the red form and turned black upon drying. This was repeated twice. For the complete removal of tellurium, the method of Lenher and Kao⁵ was used, in which hydroxylamine hydrochloride was used as the reducing agent. This purification was also repeated twice. This gave a black form of selenium. The wet selenium was washed with alcohol and vacuum dried at room temperature. This amorphous selenium was then placed in a Pyrex glass tube, connected to a vacuum pump and heated. Large volumes of gas came off, and finally a tarry mass was formed. This was allowed to cool to a shiny black, brittle solid in an atmosphere of nitrogen.

The selenium was transferred to a soft glass cylinder and melted. In this was inserted two Pyrex thermocouple wells, and a spiral heating coil of No. 30 nichrome wire. (Approximate resistance was 11 ohms.) The entire assembly was then heated in an oil-bath to 210–215°, where it was kept for several hours. It was then allowed to cool slowly in a Dewar flask filled with oil of about 225°. At the end of eight hours the temperature of the oil was still about 50°, so it was assumed that only the metallic

¹ This article is an abstract of the thesis presented by L. F. Dobry to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science.

² Regnault, *Ann. chim. phys.*, [2] 73, 51 (1840); [3] 46, 281 (1856).

³ Bettendorf and Wüllner, *Pogg. Ann.*, 133, 293 (1868).

⁴ Dewar, *Proc. Roy. Soc. (London)*, 89, 158 (1913).

⁵ Lenher and Kao, *THIS JOURNAL*, 47, 2454 (1925).

form of selenium was present. This procedure, and the assumption that only the selenium metal was present after cooling, is substantiated by Saunders and Mellor in their publications.⁶ The soft glass was then broken away, leaving a selenium slug of 32 mm. outside diameter by 60 mm. long and weighing 189.14 g. No. 30 copper wires were silver soldered to the nichrome heating element, and copper-constantan thermocouples were fixed in the wells with paraffin.

The selenium slug was suspended by fine silk thread inside a copper jacket, 4.8 cm. in diameter and 13.2 cm. long, weighing 1260 g. The thermocouple and electric heater wires from the selenium were taken out through a copper tube fastened to the lid. The entire length of the jacket was wound with No. 30 D. S. C. manganin wire, which was firmly cemented on with bakelite varnish. To the inside of the jacket was fastened a copper-constantan thermocouple. These circuits were used to adjust the temperature of the jacket equal to that of the selenium sample.

The thermostat consisted of a long Pyrex glass cylinder, 6.3 cm. in diameter by 46 cm. deep. Into the upper end was ground a 250-cc. flask which served as a stopper, and from its neck was suspended the jacket containing the selenium. The joint was sealed with de Khotinsky cement. To the sides, 10 cm. from the top, were sealed three tubes. One was connected to a mercury vapor pump, another served as an outlet for the thermocouples and heating element wires. The third tube, filled with 2.54 cm. of dibutyl phthalate, served to contain the cold junctions of the thermocouples. This cylinder, or thermostat proper, was placed in a Dewar flask, 14 cm. in diameter and 32 cm. deep, so that it could be surrounded by a suitable cooling bath. The liquid level of the bath was at least 10 cm. higher than the upper end of the copper jacket.

Electrical Standards and Experimental Technique.—A carefully prepared manganin resistance, which was frequently calibrated against a standard resistance furnished by Leeds and Northrup, was used in series with the nichrome heating coil of the selenium sample. This prepared resistance had a value of 1.0751 ohms. If E_1 and E_2 represent the volts across the nichrome heating element in the selenium, and across the standard resistance, the number of calories produced per second in the selenium is given by

$$\frac{E_1 \times E_2}{1.0751 \times 4.181}$$

In order that the voltage across the heating coil could be read on the type K potentiometer, a resistance of 1100 ohms was placed in parallel with the heating coil, and a tap taken off at about the 100 ohm value. The ratio of the tapped resistance to the entire resistance was found to be 1 : 100.84.

The thermocouples were calibrated against a platinum resistance thermometer, recently calibrated by the Bureau of Standards. The e. m. f. values for copper-constantan thermocouples given by Southard and Andrews⁷ were used as a standard. The following were the observed corrections for the two-couple thermel used in the sample.

⁶ A. P. Saunders, *J. Phys. Chem.*, **4**, 423 (1904); J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, p. 705.

⁷ Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

TABLE I
THERMOCOUPLE CORRECTIONS

Temperature of bath, °A.	84.60	151.43	209.06
Observed e. m. f., mv.	10523	7734	4469
Calculated e. m. f., mv.	10623	7798	4497
Deviation, mv.	+100	+64	+28

These deviations lie on a smooth curve fitted by the equation

$$\Delta \text{ mv.} = 3.51 (e/1000) + 0.616 (e/1000)^2$$

As thermostatic liquids in the large Pyrex Dewar flask, there were used liquid air, carbon dioxide snow and ether, carbon dioxide snow and chloroform or ice and water, depending on what temperature was desired. After a constant temperature was obtained in the slug, the apparatus was evacuated. A record of the temperature of the selenium was made until a constant change was observed. The heating current was then turned on for ten minutes, the time being measured with a stop watch to one-fifth of a second. While the current was on, the e. m. f. across the tapped resistance and the standard resistance were taken alternately every minute. At the end of ten minutes, the current was shut off, and the e. m. f. across the two-couple thermel was again taken, until a constant change of temperature was again observed. The method of Jaeger and Steinwehr⁸ was used to calculate the correction for heat lost and gained during the time that the selenium was heated and the temperature became constant. The correction amounted to about ten per cent. of the total temperature rise. These

TABLE II
DATA FOR THE HEAT CAPACITY OF SELENIUM

Temp., <i>T</i> , °A.	E. m. f. change	Temp. rise, °C.	E. m. f. across tapped resis., mv.	E. m. f. across std. res., mv.	C_p , cal./mole obs.	C_p , cal./mole calcd.
98.3	10242-9934	8.28	29415	295570	5.92	6.03
100.8	10146-9847	7.91	29399	295490	6.19	6.08
103.6	10038-9736	7.84	29415	294960	6.24	6.11
112.5	9696-9379	7.79	28973	291040	6.10	6.24
141.1	8447-8095	7.21	29065	290510	6.60	6.50
141.5	8427-8078	7.31	29081	290720	6.52	6.52
153.8	7837-7463	7.38	29153	290720	6.46	6.58
207.9	4792-4327	7.40	29904	295010	6.72	6.72
276.9	539-48	6.42	28187	275580	6.82	7.01
277.1	572-32	7.05	30154	294130	7.09	7.02
278.3	666-126	7.03	30088	293890	7.11	7.02

Ratio factor of tapped resistance, 100.837. Standard resistance, 1.07508 ohms. Weight of selenium sample, 189.14 g. = 2.388 moles.

⁸ Oswald-Luther, "Physiko-chemische Messungen," 4th ed., pp. 365-371.

corrections are included in the values of column two of Table II, in which the changes in observed microvolts are tabulated. The change in the thermocouple correction with change in temperature was also considered in calculating the temperatures, tabulated in column three of Table II. The values lie on a reasonably smooth curve, fitted by the equation

$$C_p = 2.69 + 0.0560 T - 2.66 \times 10^{-4} T^2 + 4.35 \times 10^{-7} T^3$$

The values in the last column of Table II have been calculated by the use of the above equation.

Summary

1. The heat capacity of metallic selenium was determined by the Nernst method. The selenium was carefully purified by the Lenher and Kao method.

2. The experimental values for the temperature range from 100 to 300°A. lie between 6.08 and 7.25. Values for this range have not been reported previously. The value calculated for 300°A. is approximately ten per cent. larger than that reported by Bettendorf and Wüllner.

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NOTES

The Standardization of Weights

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The method of Richards¹ for calibrating a set of weights has one particularly attractive feature, the procedure used in calculating the corrections from the system of observation equations. The discussion which follows will show that this procedure gives values which are exactly the same as the values defined by the system of equations. In other words, they are identical with the values to be found by substituting in algebraic formulas like those of Kohlrausch.²

The Reasoning of Richards.—A study of what Richards has written will explain why some do not appreciate just how accurate the calculation is. His preliminary values are *consistent* by reason of two assumptions. First, there is the assumption that the first centigram weight, called the standard of comparison, has the mass of 0.01 g. Second, it is implicitly assumed that the small differences between the masses of the various combinations of weights have been correctly measured by the rider in terms of grams. These consistent values are then translated into other terms by a method depending upon the properties of small numbers in presence

¹ T. W. Richards, *THIS JOURNAL*, **22**, 144 (1900); *Z. physik. Chem.*, **33**, 605 (1900).

² F. Kohlrausch, "Lehrbuch der praktischen Physik," 11th edition, p. 62.