[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. XVI. Heat Capacity of Cupric Oxide from 15 to 300°K.[1]

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The heat capacity of cupric oxide has been measured over the temperature range 15 to 300°K. Graphical integration of the heat capacity curve gives 10.19 ± 0.03 e.u. for the entropy at 25°. A region of reproducible high heat capacity ("hump") was found in the neighborhood of 220°K. The entropy change for the reaction $2CuO = Cu_2O + {}^1/_2O_2$ from dissociation equilibrium data was calculated by Randall, Nielsen and West to be 26.43 e.u. This value is in good agreement with the value 26.56 ± 0.15 e.u. obtained by application of the Third Law of thermodynamics. A table of thermodynamic functions for CuO has been prepared for smoothed values of temperatures.

Introduction

Millar[2] has measured the heat capacity of cupric oxide and found a non-reproducible region in the neighborhood of 220°K. More information is desirable for this undetermined region. Since considerable thermal data on the oxides of copper have been accumulated, the thermal properties of these compounds can now be intercompared. It was, therefore, desirable to measure the heat capacity of cupric oxide at low temperatures. The previous measurements on CuO at low temperatures were those of Millar[2] (from 71 to 300°K.) and of Clusius and Harteck[3] (from 30 to 200°K.).

Material and Procedure

The cupric oxide was prepared by heating electrolytic copper (99.95% purity) at 800° in a furnace through which dried air was circulated. By repeated grinding and oxidizing a fine powder (passed through No. 200 gage) was produced. The powder was then put in a porcelain dish and heated in the furnace at 700° for several days. Electrolytic analysis showed that the purity was 99.95%, corresponding to the original purity of the copper used.

"Solid calorimeter No. 6" of the group of seven vacuum calorimeters described in the first paper[4] of this series was filled with 162.030 g. (2.0363 moles) of cupric oxide for heat capacity measurements. The complete series of measurements from 15 to 300°K. showed that an anomalously high region in the neighborhood of 220°K. exists in the heat capacity curve. In order to confirm and further investigate this region, two additional series of runs were made at about 220°K. The first series of runs was started after cooling the sample very slowly to about 120°K. In the second series of runs, the sample was cooled rapidly and the readings started immediately after the temperature reached about 180°K. The results of both the supplementary runs and of the complete series indicate that, in this region, the heat capacity is wholly reproducible and leave no possible doubt concerning the existence of such an anomalously high heat capacity region in the neighborhood of 220°K.

Experimental Results

Experimental heat capacities are summarized in Table I and our data over the anomalous region 190 to 270°K. are plotted in Fig. 1 together with the results obtained by Millar[2] over the same region. In the region below 190°K., our results are uniformly lower than those of Clusius and Harteck[3] by about 3.5% between 100 and 190°K., and by an almost constant amount of 0.13 cal./mole/deg. below 100°K. Our results are, however, in close agreement with those obtained by Millar,[2] with an average deviation of less than 1%.

TABLE I

MOLAR HEAT CAPACITY OF CUPRIC OXIDE

Mol. wt. 79.57 g., 2.0363 moles

Mean T, °K.	C_p, cal./mole/deg.	Mean T, °K.	C_p, cal./mole/deg.
The complete series			
15.14	0.050	130.62	5.365
18.46	.099	138.50	5.709
20.50	.132	146.57	6.094
25.08	.248	155.84	6.511
27.84	.338	165.06	6.875
34.01	.582	174.47	7.262
37.96	0.781	183.73	7.657
45.48	1.139	192.32	8.005
51.56	1.452	200.99	8.366
57.17	1.793	209.82	8.817
60.30	1.974	218.60	9.096
65.42	2.219	227.52	9.294
71.17	2.503	235.81	9.233
77.42	2.840	243.96	9.272
84.02	3.171	253.11	9.414
90.70	3.518	262.92	9.507
97.97	3.836	272.57	9.626
105.40	4.221	282.06	9.807
112.95	4.575	289.47	9.984
121.73	4.971	297.23	10.11
The first supplementary series (slow cooling)			
196.00	8.142	231.68	9.211
204.39	8.520	240.26	9.224
213.70	8.953	248.52	9.333
222.93	9.241		
The second supplementary series (rapid cooling)			
187.12	7.779	223.76	9.263
196.44	8.156	232.53	9.219
205.38	8.553	240.96	9.244
214.58	8.991	249.12	9.330

Table II gives the heat capacity and derived thermodynamic functions for cupric oxide at selected integral values of temperature. The entropy at 298.16°K. is 10.19 e.u. of which 0.02 e.u. is contributed by extrapolation below 15°K. By Debye's T^3 law ($\theta = 310.1$°K.) Millar[2] reported a value of 9.75 ± 0.05 e.u. based on his own data from 70 to 300°K. and an extrapolation below 70°K. From the data of Millar[2] and of Clusius and Harteck,[3] Kelley[5] calculated the entropy of cupric oxide at 298.16°K. to be 10.4 ± 0.2 e.u.

Our estimate of the uncertainty in the entropy is ±0.03 e.u.; the uncertainty due to extrapolation

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(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) R. W. Millar, THIS JOURNAL, **51**, 215 (1929).

(3) K. Clusius and P. Harteck, *Z. physik. Chem.*, **134**, 243 (1928).

(4) H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

(5) K. K. Kelley, *Bull. Bur. Mines*, **447**, 44 (1950).

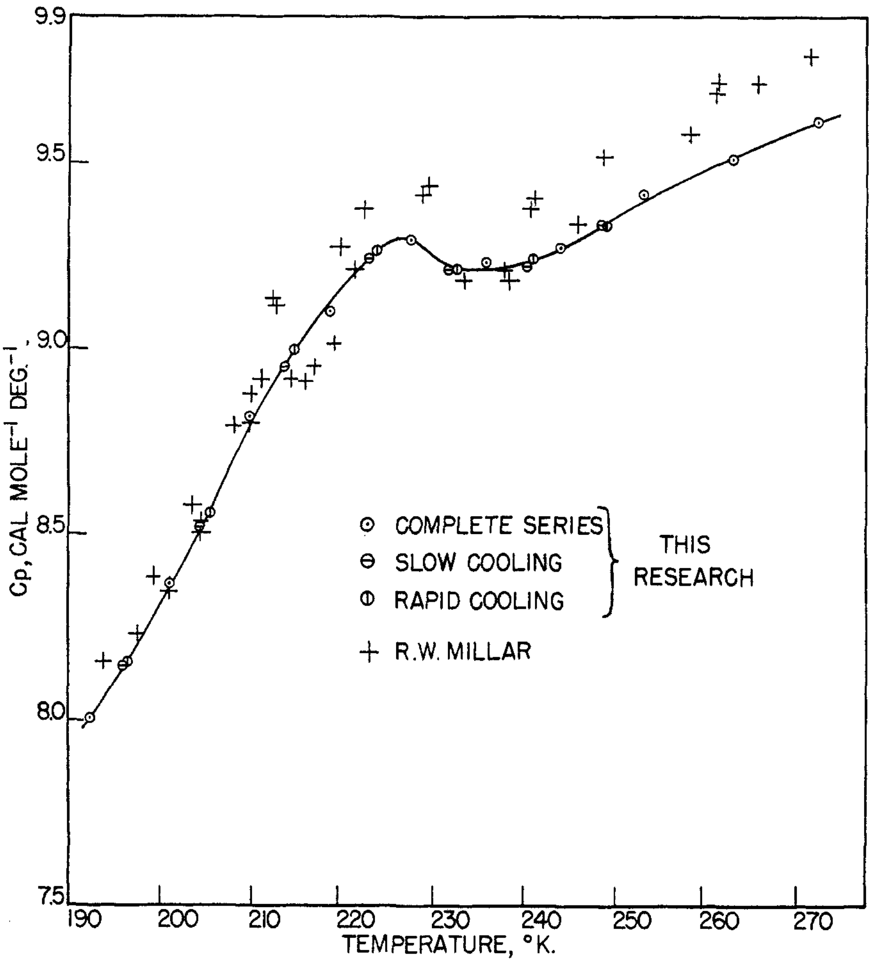

Fig. 1.—Heat capacity of cupric oxide.

below 15°K. is negligible. The heat content and the entropy due to the "hump" is estimated to be 15 cal. and 0.07 e.u., respectively.

Thermodynamic Calculations

(a) A Check on the Third Law of Thermodynamics.—A check on the third law of thermodynamics can be made by comparing the heat capacity data with the dissociation equilibrium of the $CuO-Cu_2O-O_2$ system. The dissociation pressures of cupric oxide have been carefully studied by Smyth and Roberts[6] between 880 and 1080°. They confirm the earlier results of Foote and Smith.[7] Early measurements of Debray and Joannis,[8] Moles and Paya[9] and Ruer and Nakamoto[10] are also in good agreement with the data of Smyth and Roberts.[6] Randall, Nielsen and West,[11] using the dissociation pressure data given by the above authors, Magnus'[12] heat capacity measurements on the cupric and cuprous oxides at higher temperatures (between 17 and 541°), and the heats of formation of cupric and cuprous oxides determined by Thomsen,[13] obtained the values

$$\Delta F^0 = 33{,}550 - 0.95T \ln T + 0.00375T^2 - 22.340T;$$

$$\Delta F^0_{298.16} = 25{,}610 \text{ cal.}$$

$$\Delta H^0_{298.16} = 33{,}490 \text{ cal.}$$

for the reaction $2CuO(s) = Cu_2O(s) + \frac{1}{2}O_2(g)$. From these values, we have $\Delta S^0_{298.16} = 26.43$ e.u. The value of $\Delta S^0_{298.16}$ was also computed by use of the third law of thermodynamics, from our calorimetric entropies of CuO (10.19 e.u.) and of Cu_2O[14] (22.44 e.u.) and from the spectroscopic entropy value for oxygen[15] (49.01 e.u.). This third law calculation yields

$$\Delta S^0_{298.16} = 26.56 \pm 0.15 \text{ e.u.}$$

a value which agrees within experimental error with that obtained from the dissociation pressures.

(b) Heats and Free Energies of Formation of Cupric and Cuprous Oxides.—Thomsen[13] has measured the heats of formation of cupric and cuprous oxides. He gives

$$\Delta H^0_{298.16} = -37{,}160 \text{ cal. for CuO, and}$$

$$\Delta H^0_{298.16} = -40{,}810 \text{ cal. for } Cu_2O$$

By use of the entropies of Cu,[16] O_2,[15] CuO and

TABLE II

THERMODYNAMIC FUNCTIONS FOR CUPRIC OXIDE

T, °K.	Cp, cal./mole/deg.	S^0 cal./mole/deg.	$(H^0 - H^0_0)/T$, cal./mole/deg.	$-(F^0 - H^0_0)/T$, cal./mole/deg.
16	0.064	0.021	0.016	0.005
25	0.247	.082	.061	.020
50	1.385	.567	.414	.154
75	2.714	1.385	.963	.422
100	3.947	2.337	1.557	.780
125	5.126	3.345	2.153	1.192
150	6.243	4.379	2.743	1.636
175	7.293	5.422	3.319	2.103
200	8.315	6.462	3.879	2.583
225	9.280	7.506	4.434	3.072
250	9.348	8.481	4.916	3.565
275	9.713	9.388	5.335	4.053
298.16	10.109	10.190	5.691	4.499
300	10.141	10.252	5.718	4.534

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[6] (a) F. H. Smyth and H. S. Roberts, THIS JOURNAL, **42**, 2582 (1920); (b) H. S. Roberts and F. H. Smyth, *ibid.*, **43**, 1061 (1921).

[7] H. W. Foote and E. K. Smith, *ibid.*, **30**, 1344 (1908).

[8] J. Debray and J. Joannis, *Compt. rend.*, **30**, 1344 (1908).

[9] E. Moles and S. Paya, *Anal. Soc. Espan. Fis. Quim.*, **20**, 563 (1912).

[10] R. Ruer and M. Nakamoto, *Rec. trav. chim.*, **42**, 675 (1923).

[11] M. Randall, R. F. Nielsen and G. H. West, *Ind. Eng. Chem.*, **23**, 388 (1931).

[12] A. Magnus, *Physik. Z.*, **14**, 5 (1910).

[13] J. Thomsen, "Thermochemische Untersuchungen," J. Barth, Leipzig, 1882–1886; translated by Burke "Thermo Chemistry," Longnaus, 1908.

[14] Jih-Heng Hu and H. L. Johnston, THIS JOURNAL, **73**, 4550 (1951).

[15] W. F. Giauque and H. L. Johnston, *ibid.*, **51**, 2300 (1929).

[16] W. F. Giauque and P. F. Meads, *ibid.*, **63**, 1897 (1941).

Cu_2O,[14] further relations can be obtained for them. Thus

$\Delta S^0_{298.16} = -22.28$ e.u., $\Delta F^0_{298.16} = -30{,}520$ cal. for CuO, and
$\Delta S^0_{298.16} = -18.00$ e.u., $\Delta F^0_{298.16} = -35{,}440$ cal. for Cu_2O

(c) The Standard State Entropy of Cupric Ion.—The heats of solution of cupric oxide in dilute acids were measured by Thomsen,[13] Berthelot[17] and Sabatier.[18] Their results are stated in Table III. If the salts are completely dissolved, and the solutions are dilute enough, the heat of solution, $\Delta H^0_{298.16}$ for the reaction $CuO + 2H^+ = Cu^{++} + H_2O$ should be independent of the particular acid used. This is true if we discount the value for (CuO, H_2SO_4 aq). We take the average value $\Delta H^0_{298.16} = -15.540$ cal. for this reaction. The free energy change for the same reaction may be obtained as

TABLE III

HEATS OF SOLUTION OF CUPRIC OXIDE IN DILUTE ACIDS

Solution	Heat of solution, cal. Thomsen[13]	Berthelot[17]	Sabatier[18]
(CuO, 2HCl aq)	−15,270	−15,000	−16,400
(CuO, 2HBr aq)	−15,270		−16,200
(CuO, 2HI aq)	−15,270		
(CuO, 2HNO$_3$ aq)	−15,250	−15,000	−16,200
(CuO, 2HClO$_3$ aq)	−15,910		
(CuO, 2(C$_2$H$_5$)HSO$_4$ aq)	−15,200		
(CuO, H$_2$SO$_4$ aq)	−18,800	−18,400	−19,210

$$\begin{array}{ll} Cu + 2H^+ = Cu^{++} + H_2(g) & \Delta F^0_{298.16} = 15{,}870 \text{ cal.}^{19} \\ CuO = Cu + {}^1/_2O_2(g) & \Delta F^0_{298.16} = 30{,}520 \text{ cal.} \\ H_2(g) + {}^1/_2O_2(g) = H_2O(l) & \Delta F^0_{298.16} = 56{,}700 \text{ cal.}^{20} \\ \hline CuO + 2H^+ = H_2O(l) + Cu^{++} & \Delta F^0_{298.16} = -10{,}310 \text{ cal.} \end{array}$$

So we have $\Delta S^0_{298.16} = -17.54$ e.u. for this reaction. Substituting entropies of CuO and H_2O,[21] we have

$$S^0_{Cu^{++}} = -24.1 \text{ e.u. at } 298.16\,^\circ\text{K.}$$

Latimer, Pitzer and Smith[22] have obtained −25.9 ± 3.0 e.u. and −26.6 ± 1 e.u., respectively, as values of the entropy of $Cu^{++}(aq)$ from data for the reactions $Cu(s) + 2H^+(aq) = Cu^{++}(aq) + H_2(g)$ and $Cu(s) + 2\,Ag^+(s) = Cu^{++}(aq) + 2Ag(s)$.

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(18) P. Sabatier, *Compt. rend.*, **125**, 301 (1897).

(19) From standard oxidation–reduction potential of Cu, Cu^{++}. The value is taken as −0.344 v. from W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1951.

(20) F. D. Rossini, *J. Research Natl. Bur. Standards*, **22**, 407 (1939).

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(22) W. M. Latimer, K. S. Pitzer and W. V. Smith, *ibid.*, **60**, 1829 (1938).

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The Use and Limitations of Heterogeneous Rate Constants in Polarographic Kinetics

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The use of first-order heterogeneous rate constants is practicable only if the diffusion of the depolarizer from the bulk of the solution (kinetic waves) or of the electrode product from the drop surface (catalytic waves) is negligibly small. In such cases the expression for the conversion factor derived by previous authors is valid. The restriction does not preclude control of the kinetic current by the diffusion of a non-electrolyzable species. It is indicated to what degree the true conversion factor departs from the derived value when the restriction is not obeyed. The heterogeneous rate constant method is applied to a novel type of reaction. Also, the use of the factor $\sqrt{7/3}$ is discussed, and the behavior of the rising portion of kinetic waves derived.

It is the purpose of this article to investigate the conditions under which first-order kinetic phenomena at the dropping mercury electrode (d.m.e.) may be interpreted by the use of heterogeneous or surface rate constants.[1,2] These constants, denoted $(k)_h$, have the units cm. sec.$^{-1}$, and are often incorporated into equations as μk[3–5] or δk,[1,6] where k is the conventional first-order rate constant and μ or δ a factor of unit cm. Equations for reaction-affected currents are much simpler if expressed in terms of $(k)_h$ than k; consequently heterogeneous constants have been used almost exclusively in the past. The value of μ can be determined rigorously by equating the two current expressions based on the two rate constants and solving for μ directly. This has been done in several instances, and μ found to be given by a relatively simple expression; but the conditions that must be generally satisfied if the expression is to hold, and hence the restrictions that must be placed on the use of $(k)_h$ as a substitute for k, have not been adequately stated. Although the conclusions arrived at here are valid only for first-order rate constants, in practice the reactions usually involve two reactants, one of which is maintained at a constant concentration.

The Kinetic Current.—In a recent article,[7] Delahay has discussed the system

$$A \underset{k_b}{\overset{k_f}{\rightleftarrows}} B \qquad (1)$$

in which B is a species that depolarizes the d.m.e. and A is a species that does not. It was shown that if k_f is so small that the surface concentration of A is the same as the bulk concentration, the current

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(1) Paul Delahay, THIS JOURNAL, **73**, 4944 (1951).

(2) Paul Delahay, *ibid.*, **74**, 3506 (1952).

(3) K. Wiesner, *Z. Elektrochem.*, **49**, 164 (1943).

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(5) R. Brdička and K. Wiesner, *ibid.*, **12**, 39, 138 (1947).

(6) Paul Delahay and Jacob E. Strassner, THIS JOURNAL, **73**, 5269 (1951).

(7) Paul Delahay, *ibid.*, **74**, 3506 (1952).