double layer, which means that the hump is caused by variations in C_1 rather than in C_2, as mentioned above.

The series resistance of octyl alcohol-covered surfaces at no time varied inversely as the square root of the frequency. Since this was the behavior of the polarization resistance of non-polarizable or partially polarized electrodes observed by Jones and Christian, it may be assumed that their polarization resistances were not caused primarily by the presence of surface-active substances. Other less direct types of evidence might be cited to substantiate this conclusion. The most probable cause of true polarization resistance is therefore the concentration polarization first treated in this connection by Warburg.[16,27] Our results have shown that this effect is negligible in ideal polarized electrodes. The fact that the "polarization capacity" of non-polarizable electrodes fails to obey Warburg's equation with accuracy is undoubtedly to be ascribed, at least in part, to the additional presence of the ordinary double layer capacity, not caused by polarization. The term "polarization capacity" ought, therefore, to be limited to that part of the capacity of a non-polarizable electrode attributable to the concentration polarization which accompanies the flow of alternating current across its metal-solution phase boundary. This quantity appears not yet to have been measured, except in a few cases where the double layer capacity was relatively very small.[11]

Conclusion and Acknowledgment

The experiments described in this paper show that when suitable techniques are used the electrical characteristics of the double layer do not exhibit any anomalous behavior. This result makes it possible to interpret measurements on the capacity of the double layer in a satisfactory manner and to correlate these measurements with other types of electrocapillary measurements.

It is a pleasure to express my gratitude to the American Philosophical Society for financial support during the course of this work and to Ruth Levin Merblum for valuable technical assistance.

Summary

1. Theoretical considerations show that the effect of frequency on the capacity and resistance of a clean ideally polarized electrode should be negligible.

2. Experimental studies on mercury surfaces confirm this conclusion.

3. There is no slow step in the formation of the electrical double layer even when surface-active ions are present.

4. On octyl alcohol-covered mercury surfaces the capacity and resistance vary in a complex manner which can be understood by assuming the octyl alcohol layer to have an electrical resistance whose magnitude depends upon the potential.

5. Significant errors arise in the measurement of capacity and resistance when the electrical resistance from every element of the surface to the reference electrode is not the same.

6. On clean polarized mercury surfaces the polarization resistance of the double layer is zero within the probable experimental error.

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[27] Warburg's equation led to the variation of polarization resistance with frequency observed by Jones and Christian.

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Specific Heats at Low Temperatures of TiO, Ti_2O_3, Ti_3O_5, and TiN[1]

BY C. HOWARD SHOMATE[2]

The thermochemical properties of the titanium oxides and nitride are of interest in the production of ferrotitanium from titanium ores and in the refining of steels. The Pacific Experiment Station of the Bureau of Mines has undertaken a program to obtain certain thermodynamic data for these compounds and related substances. This paper presents low-temperature specific heat and entropy data for the monoxide, sesquioxide, tritapentoxide and mononitride of titanium. No such data have been reported previously for any of these substances; however, McDonald and Seltz[3] have made measurements on rutile, a form of titanium dioxide.

Experimental

Materials

Titanium monoxide was prepared by the reaction of equimolal quantities of titanium dioxide and titanium metal at 1,350° *in vacuo*. Analysis of the product showed it to be 99.2% titanium monoxide, 0.1% titanium carbide and 0.7% silicon. The sample used in the measurements weighed 223.24 g.

Titanium sesquioxide was prepared by the carbon reduction of the dioxide, according to the reaction: $2TiO_2 + C \rightarrow Ti_2O_3 + CO$. The finely ground reaction mixture was heated *in vacuo* to 1,400° for twenty hours. Analysis showed 99.4% Ti_2O_3, 0.3% TiC, and 0.3% SiO_2. A 175.87-g. sample was used in the measurements.

Titanium tritapentoxide was prepared also by the carbon reduction of titanium dioxide. The reaction, $3TiO_2 + C \rightarrow Ti_3O_5 + CO$, was carried out *in vacuo* at 1,350° for eight hours. Analysis of the product gave 99.1% Ti_3O_5, 0.2% TiC and 0.7% SiO_2. The measurements were made on a 137.32-g. sample.

Titanium nitride was prepared by passing a stream of

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Chemist, Pacific Experiment Station.

[3] McDonald and Seltz, THIS JOURNAL, **61**, 2405 (1939).

purified nitrogen and hydrogen over titanium metal at 1,400°. Analysis indicated a purity of at least 99.5%, the principal impurity being a compound of silicon, probably silicon nitride. The sample used in the measurements weighted 201.18 g.

X-Ray diffraction measurements on the sesquioxide and tritapentoxide were made by Dr. E. V. Potter.[4] The sesquioxide showed a pattern similar to ferric oxide, and although the lines in the pattern for the tritapentoxide were weak and fuzzy, they did not correspond with those of any of the other titanium oxides.

Specific Heats

The method and apparatus used in the low-temperature specific heat measurements have been described previously.[5,6] The experimental results, expressed in defined calories (1 calorie = 4.1833 int. joules),[7] are listed in Table I and shown graphically in Fig. 1. The values of the specific heats at 298.16°K., obtained by extrapolation of a smooth curve through the experimental points, also are included in Table I. The molecular weights are in accordance with the 1941 International Atomic Weights. Corrections were made in the specific heat results of the oxides for the impurities mentioned above. No correction was made for the impurity in titanium mononitride, as the necessary low-temperature specific heat data for making the correction are not available; however, the application of such a correction probably would change the results by less than the experimental uncertainty.

TABLE I

SPECIFIC HEATS

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
TiO, mol. wt. = 63.90		Ti_3O_5, mol. wt. = 223.70		TiN, mol. wt. = 61.91	
52.6	0.751	53.1	2.877	52.5	0.527
56.7	0.912	56.9	3.406	56.4	0.655
60.6	1.080	61.0	4.034	60.5	0.809
64.8	1.271	65.4	4.723	64.7	0.974
69.7	1.504	69.6	5.445	69.7	1.189
74.2	1.728	75.0	6.385	74.1	1.384
78.6	1.948	79.4	7.176	78.5	1.582
84.5	2.248	83.9	7.999	85.3	1.892
96.9	2.886	94.1	9.887	94.9	2.331
105.7	3.341	104.3	11.82	104.6	2.781
115.1	3.819	115.1	13.87	115.2	3.263
125.1	4.315	125.2	15.76	125.2	3.704
135.1	4.799	135.1	17.55	135.1	4.141
145.8	5.283	145.8	19.40	145.8	4.577
155.4	5.703	155.7	20.99	155.6	4.977
165.5	6.112	165.7	22.58	165.7	5.358
176.2	6.523	175.6	24.12	175.7	5.735
185.9	6.867	185.7	25.47	185.7	6.073
196.3	7.208	195.9	26.79	196.1	6.410
205.8	7.519	205.5	28.06	206.0	6.705
215.8	7.807	216.1	29.29	216.3	7.018
226.1	8.075	226.1	30.34	226.3	7.286
235.8	8.308	235.8	31.29	235.9	7.520
246.2	8.546	246.0	32.32	246.0	7.768
256.2	8.788	256.1	33.30	256.0	8.008
266.2	8.984	266.2	34.20	266.1	8.234
276.2	9.166	276.3	35.07	276.4	8.448
286.1	9.341	286.3	35.99	286.2	8.642
296.3	9.521	296.6	36.88	296.4	8.830
(298.16)	(9.55)	(298.16)	(37.00)	(298.16)	(8.86)
Ti_2O_3, mol. wt. = 143.80					
53.0	1.471	125.2	9.382	235.7	20.12[a]
57.0	1.775	135.2	10.58	235.8	20.14[a]
61.1	2.129	145.6	11.79	240.3	20.67[a]
65.4	2.516	155.5	12.92	244.7	20.56[a]
69.7	2.932	165.5	13.98	246.2	20.60
74.3	3.395	175.6	15.03	256.0	21.14
78.8	3.873	185.6	15.95	266.1	21.67
85.6	4.623	195.9	16.87	276.2	22.21
94.8	5.682	205.9	17.74	286.1	22.70
106.4	7.081	216.2	18.58	296.4	23.18
115.2	8.168	226.2	19.33	(298.16)	(23.27)

[a] Specific heat values affected by the "hump."

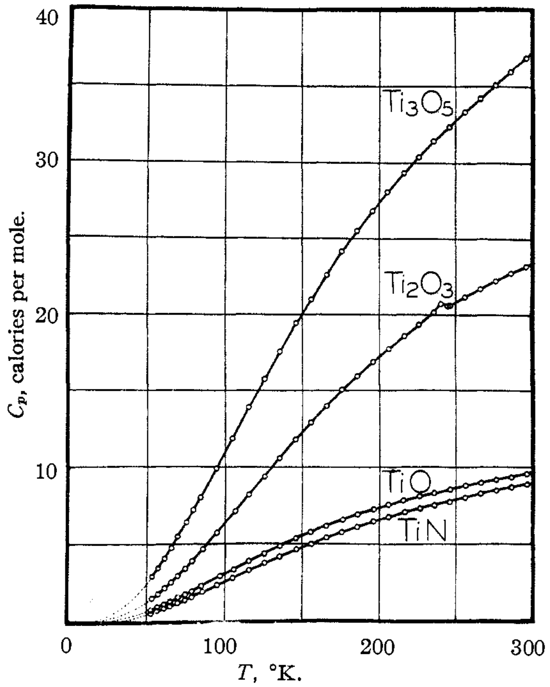

Fig. 1.—Specific heats.

All weights were corrected to vacuum, using the following densities: titanium monoxide, 4.92; titanium sesquioxide, 4.56; titanium tritapentoxide, 4.15; and titanium mononitride, 5.24. Density determinations were made in this laboratory by R. J. O'Dea.[2]

With the exception of a small "hump" in the specific heat curve of titanium sesquioxide, the peak occurring about 242°K., the substances exhibited normal behavior in the temperature range studied.

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(4) Physicist, Salt Lake City Station, Bureau of Mines.

(5) Kelley, THIS JOURNAL, **63**, 1137 (1941).

(6) Shomate and Kelley, *ibid.*, **66**, 1490 (1944).

(7) Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

Entropies

The evaluation of the entropy at 298.16°K. is obtained by graphical integration of a plot of C_p against log T. This necessitates the extrapolation of the specific heat curve from the temperature of the lowest measurement down to the absolute zero of temperature. It was found that the following function sums adequately represent the measured specific heats in the temperature ranges indicated.

$$\mathrm{TiO}:\quad D\left(\frac{437}{\mathrm{T}}\right) + E\left(\frac{653}{\mathrm{T}}\right) \quad (1\%,\ 50\text{–}298°\mathrm{K.})$$

$$\mathrm{Ti_2O_3}:\quad 2D\left(\frac{441}{\mathrm{T}}\right) + 3E\left(\frac{663}{\mathrm{T}}\right) \quad (1\%,\ 50\text{–}225°\mathrm{K.})$$

$$\mathrm{Ti_3O_5}:\quad 3D\left(\frac{399}{\mathrm{T}}\right) + 5E\left(\frac{654}{\mathrm{T}}\right) \quad (2\%,\ 50\text{–}298°\mathrm{K.})$$

$$\mathrm{TiN}:\quad {}^1/_2E\left(\frac{273}{\mathrm{T}}\right) + D\left(\frac{927}{\mathrm{T}}\right) + {}^1/_2E\left(\frac{580}{\mathrm{T}}\right) \quad (2\%,\ 50\text{–}298°\mathrm{K.})$$

The symbols D and E denote, respectively, Debye and Einstein functions. These functions were used for extrapolating the specific heat curves to 0°K.

The total heat absorption in the region of the "hump" in titanium sesquioxide at 242°K. was obtained by summing the energies of three successive specific heat determinations in the manner described by Shomate.[8] The excess energy in the "hump," above that calculated from a smooth "normal" curve drawn through this region, is only 3.6 cal./mole, and the excess entropy 0.015 e.u./mole.

Table II summarizes the entropy calculations for the four substances.

TABLE II

ENTROPIES AT 298.16°K. (E. U./MOLE)

	TiO	Ti_2O_3	Ti_3O_5	TiN
0–52.00° K.	0.25	0.50	0.97	0.13
52.00–298.16° K.	8.06	18.33	29.95	7.07
	8.31 ± 0.04	18.83 ± 0.06	30.92 ± 0.10	7.20 ± 0.04

Summary

Specific heats of the monoxide, sesquioxide, tritapentoxide and mononitride of titanium were measured in the temperature range 52 to 298°K. Titanium sesquioxide has a small "hump" in its specific heat curve, the maximum being at 242°K. There is only 0.015 e.u./mole of excess entropy in the "hump," above the "normal" curve.

The following molal entropies at 298.16°K. were computed: titanium monoxide, 8.31 ± 0.04; titanium sesquioxide, 18.83 ± 0.06; titanium tritapentoxide, 30.92 ± 0.10 and titanium mononitride, 7.20 ± 0.04.

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[8] Shomate, *Ind. Eng. Chem.*, **36**, 910 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of the Hydrides of Boron. VII. Beryllium Borohydride, BeB_2H_8

BY G. SILBIGER AND S. H. BAUER

Of the three metallo borohydrides prepared by H. I. Schlesinger[1] and his co-workers, an electron diffraction study of aluminum borohydride has already been carried through.[2] In this paper, the results of a similar investigation of the beryllium compound and further work on aluminum borohydride are reported. A probable configuration for the beryllium compound has been deduced and the interatomic distances in that molecule have been estimated. The $Be(BH_4)_2$ was furnished by Dr. H. C. Brown, to whom we wish to express our sincere appreciation.

TABLE I

Max.	Min.	s_0	Inten.	$s_c(D_2)$	s_c/s_0
1		1.57	8	1.37	(0.873)
	2	3.52	−5	3.20	(.909)
2		4.47	8	4.37	.978
	3	5.35		5.20	.972
3		6.05		6.00	.992
	4	6.60	−2	6.50	.985
4		7.56	3	7.45	.985
	5	9.54	−1	9.35	.980
5		11.97	1	11.43	.955
				Av.	.978
				Av. dev.	.008

The sample was transferred, by sublimation, to a metal, high temperature nozzle and electron diffraction pictures of varying densities were obtained with the material between 40 and 50° (reported vapor pressure at 45° is 37.1 mm.).[1b] The visually estimated diameters and intensities are listed in Table I. We were unable to measure accurately the diameter of the shoulder to the left of the third peak and hence the position indicated for the maximum on the observed intensity curve is approximate. A radial distribution curve (Fig. 1, R. D.) was computed following the method of Walter and Beach.[3] It shows principal peaks at 1.73, 2.71 and 3.41 Å. Since these

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[1] (a) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **62**, 3421 (1940); (b) A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940), (c) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

[2] J. Y. Beach and S. H. Bauer, THIS JOURNAL, **62**, 3440 (1940).

[3] J. Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940).