at 63.5°K. resulting from the addition of small volume increments. This is included in Fig. 4.

The heterogeneity of the surface is reflected in the exponential decrease of population of the sites with the increase in energy for the sites of high energy in the equilibrium curve. However, it is interesting to note that the bulk of the sites are grouped in an energy band which is not more than five hundred calories wide. One would expect a distribution of this type for a surface consisting predominantly of sites derived from the possible crystal faces for titanium dioxide.[8]

The distributions are based essentially on a simple model of unimolecular, localized adsorption with negligible molecular interaction. At coverages above 0.5 of a monolayer, the inflection point in the curve for the differential heat is probably caused by the appearance of attractive molecular interaction. Consequently, the simple model used above is inadequate and, at coverages approaching the monolayer capacity, the distribution curve would require a more detailed interpretation.

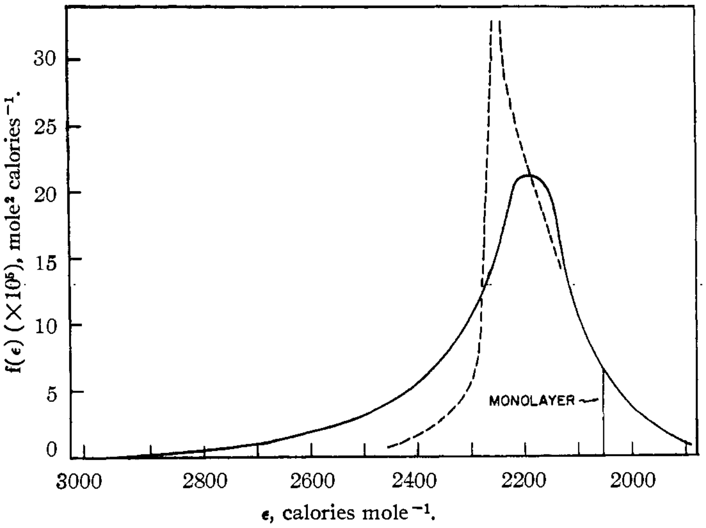

Fig. 4.—Energy distribution for argon adsorbed on rutile: — equilibrium distribution; ---. non-equilibrium distribution.

**Acknowledgment.**—We are indebted to Dr. Walter K. Nelson of the National Lead Company for the sample of titanium dioxide and also for pertinent data on the sample. The drawings and figures in the paper were made by Charles S. Baughman. A Frederick Gardner Cottrell grant from the Research Corporation aided the work. Some of the necessary associated apparatus used in the work is the property of the Atomic Energy Commission (Contract No. AT(30-1)-824).

CLEVELAND, OHIO

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[8] Dr. Walter K. Nelson of the National Lead Company has informed us that the titanium dioxide used is acicular and shows a predominance of 100 and 110 planes.

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

# Low-temperature Heat Capacities and Entropies at 298.16°K. of Manganese Sesquioxide and Niobium Pentoxide

BY E. G. KING

RECEIVED FEBRUARY 6, 1954

Low temperature heat capacity measurements of manganese sesquioxide ($Mn_2O_3$) and niobium pentoxide ($Nb_2O_5$) were conducted throughout the temperature range 51–298°K. The heat capacity of manganese sesquioxide shows a pronounced maximum at 79.4°K. The entropies at 298.16°K. are 26.4 ± 0.5 cal./deg. mole for manganese sesquioxide and 32.8 ± 0.2 cal./deg. mole for niobium pentoxide.

This paper reports heat capacity measurements throughout the temperature range from 50 to 298°K. and entropy evaluations of crystalline manganese sesquioxide ($Mn_2O_3$) and niobium pentoxide ($Nb_2O_5$). No previous similar data exist for either of these substances, except a rather uncertain value of the entropy of manganese sesquioxide derived from dissociation pressure data by Kapustinsky and Bayuskina.[1] Data for manganese oxides of composition MnO, $Mn_3O_4$ and $MnO_2$ were published previously from this Laboratory.[2-4]

## Materials

The manganese sesquioxide was part of the sample described by Orr[5] and used by him in high temperature heat content measurements. It analyzed 69.64% manganese and 10.13% available oxygen, as compared with the theoretical 69.59 and 10.14%. The X-ray diffraction pattern showed only lines corresponding to those for bixbyite as listed in the A.S.T.M. catalog.

The niobium pentoxide also was described by Orr.[6] The impurities, estimated spectrographically, totaled less than 0.10%. X-Ray diffraction showed the substance to be the high-temperature modification reported by Brauer.[7]

## Measurements and Results

The heat capacity measurements were conducted with previously described[8] apparatus and methods. The results are expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole. Molecular

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[5] R. L. Orr, *ibid.*, **76**, 857 (1954).

[6] R. L. Orr, *ibid.*, **75**, 2808 (1953).

[7] G. Brauer, *Z. anorg. Chem.*, **248**, 1 (1941).

[8] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

weights accord with the 1951 International Atomic Weights[9] and all weighings were reduced to vacuum. The sample masses used in the measurements were 211.11 g. of manganese sesquioxide and 213.91 g. of niobium pentoxide.

The experimental heat capacity values are listed in Table I and plotted in Fig. 1. The heat capacity of niobium pentoxide follows a regular course and requires no discussion. That of manganese sesquioxide exhibits a pronounced peak with the maximum at 79.4°K. The heat capacity at the maximum is more than 12.8 cal./deg. mole, as compared with a "normal" value of about 8.7 at this temperature. To obtain the shape of the peak, the results labeled (a) in Table I were measured without temperature gaps and with temperature rises near the maximum of only 0.952 to 1.079°. As is usual, the curve rises to the maximum from the low temperature side much less abruptly than it falls on the high temperature side. Similar peaks have been observed for manganese dioxide[3] and manganous oxide,[4] and also for manganous sulfide,[10] selenide,[11] telluride[11] and fluoride.[12]

Table I

Heat Capacities

| $T$, °K. | $C_p$, cal./deg. mole | $T$, °K. | $C_p$, cal./deg. mole | $T$, °K. | $C_p$, cal./deg. mole |
|---|---|---|---|---|---|
| | | $Mn_2O_3$ (mol. wt. 157.86) | | | |
| 54.39 | 5.676 | 83.68 | 9.057 | 206.31 | 19.34 |
| 58.81 | 6.494 | 84.27 | 9.051(a) | 216.43 | 20.06 |
| 63.23 | 7.476 | 95.17 | 9.686 | 228.60 | 20.89 |
| 67.51 | 8.551 | 104.60 | 10.39 | 237.35 | 21.45 |
| 71.77 | 9.815 | 114.70 | 11.37 | 246.09 | 22.06 |
| 75.32 | 11.13(a) | 124.51 | 12.31 | 256.10 | 22.76 |
| 75.94 | 11.48 | 135.88 | 13.40 | 266.35 | 23.53 |
| 77.28 | 12.08(a) | 146.36 | 14.38 | 276.01 | 24.15 |
| 78.28 | 12.82(a) | 155.68 | 15.23 | 286.36 | 24.93 |
| 79.33 | 12.32(a) | 166.07 | 16.15 | 296.25 | 25.59 |
| 79.98 | 10.67 | 176.08 | 17.01 | 298.16 | (25.73) |
| 80.39 | 9.467(a) | 185.97 | 17.83 | | |
| 81.92 | 9.131(a) | 196.09 | 18.58 | | |
| | | $Nb_2O_5$ (mol. wt. 265.82) | | | |
| 53.24 | 5.127 | 114.54 | 15.39 | 216.60 | 26.54 |
| 57.12 | 5.716 | 124.62 | 16.85 | 228.17 | 27.40 |
| 61.25 | 6.426 | 136.03 | 18.42 | 236.41 | 27.98 |
| 65.58 | 7.206 | 146.39 | 19.76 | 245.82 | 28.57 |
| 70.06 | 7.977 | 155.98 | 20.89 | 256.19 | 29.20 |
| 74.52 | 8.732 | 166.28 | 22.04 | 266.49 | 29.81 |
| 80.17 | 9.721 | 176.36 | 23.06 | 276.76 | 30.44 |
| 84.45 | 10.48 | 186.11 | 24.02 | 286.50 | 30.98 |
| 94.75 | 12.21 | 196.13 | 24.88 | 296.64 | 31.45 |
| 104.36 | 13.76 | 206.15 | 25.69 | 298.16 | (31.57) |

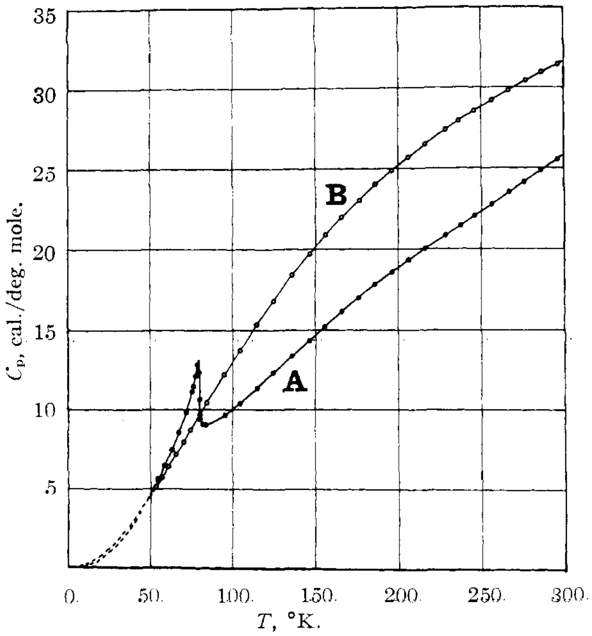

Fig. 1.—Heat capacities: curve A, $Mn_2O_3$; curve B, $Nb_2O_5$.

A separate determination was made of the total heat absorption by manganese sesquioxide between 73.20 and 88.00°K., the result being 152.11 cal./mole. Of this amount, 96.63 cal./mole is absorbed between 75.00 and 84.00°K., giving a mean heat capacity of 10.74 cal./deg. mole for the 9° interval surrounding the maximum. The heat absorption for the interval 75.00 to 84.00°K. also was obtained from summation ($\Sigma = C_p\Delta T$) of the results labeled (a) in Table I, which gave 96.56 cal./mole, in good agreement with the more direct measurement.

## Entropies at 298.16°K.

The entropy calculation of manganese sesquioxide for the measured temperature range (51–298.16°K.) was divided into three parts, corresponding to the temperature intervals 51–75, 75–84, and 84–298.16°K. Entropy increments for the intervals 51–75 and 84–298.16°K. were obtained by Simpson-rule integrations of plots of $C_p$ against log $T$, the results being, respectively, 2.860 and 20.235 cal./deg. mole. The entropy increment for the interval 75–84°K. was obtained from the measured total heat absorption (96.63 cal./mole) and the effective average temperature evaluated from the results labeled (a) in Table I. The effective average temperature was computed as the ratio of $\Sigma C_p\Delta T$ to $\Sigma C_p\Delta T/T$ for the interval, the result being 79.15°K. This gives 96.63/79.15 = 1.221 cal./deg. mole. The total measured portion of the entropy is, therefore, 24.32 cal./deg. mole.

Computation of the extrapolated portion of the entropy (0–51°K.) was difficult because of the short temperature interval covered by the experimental heat capacity values below the maximum at 79.4°K. The procedure adopted was to fit the heat capacity curve well above the maximum by a sum of empirical Debye and Einstein functions and then smoothly merge the measured results below 79.4°K. into this function sum. The sum, $D(187/T) + 2E(376/T) + E(603/T) + 2E(1143/T)$, was found to fit the experimental heat capacities between 115 and 250°K. with a maximum deviation of 1.3%. The curve through the measured heat-capacity values merged smoothly into this function sum at 29.51°K. This procedure gave 2.08 cal./deg. mole as the extrapolated portion of the entropy.

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(11) K. K. Kelley, *ibid.*, **61**, 203 (1939).

(12) J. W. Stout and H. E. Adams, *ibid.*, **64**, 1535 (1942).

The entropy increment for niobium pentoxide between 51 and 298.16°K. was obtained by Simpson-rule integration of a $C_p$ against log $T$ plot. The extrapolated increment, below 51°K., was calculated using the Debye and Einstein function sum, $D(163/T) + 2E(311/T) + 2E(489/T) + 2E(970/T)$, which fits the experimental heat capacity data over the entire measured range with a maximum deviation of 0.6%. The entropy results appear in Table II.

The measured portions of the entropy constitute about 92% of the totals at 298.16°K. The limit of error assigned to the manganese sesquioxide value is larger than usual to allow for extra uncertainty in extrapolation below 51°K.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

| | $Mn_2O_3$ | $Nb_2O_5$ |
|---|---|---|
| 0–51°K. (extrap.) | 2.08 | 2.51 |
| 51–298.16°K. (meas.) | 24.32 | 30.30 |
| $S^0_{298.16}$ | 26.4 ± 0.5 | 32.8 ± 0.2 |

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY]

# Electrode Potentials in Molten Silicates

BY ROSTISLAV DIDTSCHENKO[1] AND EUGENE G. ROCHOW

RECEIVED FEBRUARY 12, 1954

A reversible oxygen electrode has been developed for investigating the activity of oxide ion in solutions of metal oxides in molten lead silicate. Operation of the electrode in the system $Pt:O_2$/standard glass//standard glass + $R_xO_y/O_2:Pt$ provides a series of potentials which vary with the basicity of the oxide $R_xO_y$ as well as with its concentration. The regular dependence of potential upon the size, the charge, and the electronic structure of the dissolved metal ion is considered in terms of the random-network theory of glasses.

The crystallographic investigations of Bragg and Pauling have established that solid silicates are predominantly ionic substances the structures and properties of which are determined by the charges, sizes and proportions of the ionic constituents. It was suggested by Zachariasen[2] that similar factors must be operative in the formation of glasses in general, and of silicate glasses in particular. This assumption was confirmed by the X-ray investigations of Warren and his school,[3] which led to the formulation of the so-called "random-network theory of glasses" in its present form. According to this theory the silicate glasses consist of an irregular network of $SiO_4$ tetrahedra with short-range crystallographic order. The remaining cations are statistically distributed in the holes of that network in such a way that they are coördinated with an optimum number of single-bonded oxygen ions from the silicate network.

Glasses have always been considered to be undercooled liquids, and hence it seems justifiable to assume that the internal structure of a silicate melt must be very similar to that of the solid glass obtained from it. In such a silicate glass, oxygen ion is a predominant constituent. Furthermore, the activity of oxygen ion in silicate melts is primarily responsible for their acidic or basic behavior. A detailed knowledge of oxygen ion activity therefore is important from the theoretical point of view. Since there is very little general information about the activities of the constituents of silicate melts, we thought it interesting and useful to develop a method of measuring the oxygen ion activity in a simple silicate system, with special emphasis upon the changes of this activity due to the presence of dissolved metal oxides.

The problem is analogous to $p$H measurements in aqueous solution, and the obvious way of tackling it would be to use an electrode that responds reversibly to oxygen ion activities, as in an oxide concentration cell consisting of molten silicates. It has been shown that the platinum–oxygen electrode at 800–1000° is reversible to oxygen and to oxide ion in molten carbonates,[4] borates[5] and sulfates.[6] Thus we had reason to believe that the platinum–oxygen electrode should also be applicable to molten silicates, if the experimental difficulties could be mastered.

We set out to measure the e.m.f. of the cell type

$$Pt:O_2/\text{silicate solvent}//\text{silicate solvent} + M_xO_y/O_2:Pt$$

where $M_xO_y$ designates an oxide dissolved in a simple silicate. Lead silicate of the composition $PbO \cdot SiO_2$ was selected as the solvent because of its advantageous properties such as low melting point and excellent glass-forming ability with other oxides. For obvious reasons, in the future we shall refer to this lead silicate as our "standard glass."

## Experimental

The standard glass was prepared by melting in a platinum crucible an intimate mixture of dry lead oxide and silica in an electric muffle furnace under oxygen at 850–900° and quenching the resulting melt to a solid glass. All other glasses were made in the same way by previously adding to the standard glass mixture the exactly weighed amount of an oxide, carbonate or nitrate so as to give a glass having the desired concentration of the oxide under investigation. All substances used were of analytical purity.

The construction of the cell created considerable difficulty. Several designs constructed from alundum and magnesia were tried without success; the alundum was strongly attacked by molten silicates, and the magnesia crucibles available to us had good chemical resistivity but were either too porous or too dense. The construction finally adopted used two identical porous porcelain cups which were fired previously at the sintering temperature (1200°) in a gas furnace. The insides of the cups were lined with platinum

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(1) Natvar Fellow at Harvard University in 1952–1953.

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