mole^{-1} for $\theta = 0.13$, ±0.6 cal. deg.$^{-1}$ mole^{-1} for $\theta = 0.23$ and ±0.3 cal. deg.$^{-1}$ mole^{-1} for $\theta = 0.40$. Most of this uncertainty comes from the heat capacity measurements.

The results indicate strongly that thermodynamic equilibrium has not been attained between the surface and the adsorbed krypton. The experimental procedure which was used as well as theoretical considerations lead one to believe that most of the randomness in the system existing at approximately 50°K. was preserved at temperatures below this value. From the standpoint of the experimental procedure in cooling which was followed, the relatively rapid cooling of the calorimeter from 50 to 12°K. prior to heat capacity measurements appears to be the most likely step during which equilibrium may not have been attained. If we accept as a reasonable model for the adsorbed gas one for which the molecules are adsorbed in monomolecular fashion on a heterogeneous surface and molecular interaction is neglected, it is possible to calculate the configurational entropy by the theoretical method developed by Hill.[5] Drain and Morrison[6] have utilized this method in their interpretation of the results of the argon–rutile system. Following essentially the same method as Drain and Morrison, we have used the continuous distribution of energy at the adsorption sites shown in Fig. 2 to compute values of the configurational entropy at 60°K. For coverages of 0.23 and 0.40 monolayers, these are 1.27 and 1.06 cal. deg.$^{-1}$ mole^{-1}. These theoretical results appear to be consistent with the experimental picture.

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CLEVELAND, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY[1]]

Low Temperature Heat Capacity and Entropy of Molybdenum Trioxide and Molybdenum Disulfide

BY D. F. SMITH,[2] DUANE BROWN,[3] A. S. DWORKIN, D. J. SASMOR AND E. R. VAN ARTSDALEN

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The heat capacities of crystalline MoS_2 and MoO_3 have been measured down to about 18°K. Both substances have layer-lattice structure and exhibit approximately T^2 dependence of C_p between 20 and 60°K. Because of the T^2 behavior prior extrapolations by the T^3 law below 50°K. are in error. Corrected values are given for S^0 and $\Delta H^0{}_f$.

A number of anisotropic substances which crystallize with so-called layer-lattice structure have been shown to exhibit a T^2 dependence of their heat capacity in the approximate range 15 to 60°K.[4-6] Theories concerning this behavior have been published by Tarassov,[7] Komatsu and Nagamiya,[8] Krumhansl and Brooks,[9] Rosenstock[10] and Newell.[11] The detailed interpretation of the observed approximate T^2 behavior in the low temperature range is still the subject of controversy. We therefore chose for study several additional compounds with layer structure. It has been shown by several of us[12] that the anisotropy in the cadmium iodide layer structure is insufficient to cause T^2 behavior of the heat capacity above 15°K., below which the measurements did not extend.

Two molybdenum compounds, the disulfide and trioxide, are good examples of layer lattice structures in polyatomic compounds and are, therefore, well suited to low temperature heat capacity investigations in connection with T^2 behavior. Molybdenum disulfide, MoS_2, the "moly" of commerce, has so marked a layer structure that it is slippery to the touch. This is true of both the natural mineral (molybdenite) and artificial preparations. MoS_2 and probably WS_2 are the only examples of sixfold coördinated layer structure in which the coördination is not octahedral; molybdenum disulfide is hexagonal with elongated bimolecular[13] units. Sulfur atoms lie at corners of right equilateral trigonal prisms which share vertical edges to build up MoS_2 layers normal to the C-axis. Molybdenum trioxide, MoO_3, is a white orthorhombic substance possessing fewer layer properties on the macroscopic scale, although it does cleave well parallel to certain

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(1) Operated by Union Carbide Nuclear Company, formerly by Carbide and Carbon Chemicals Co., for the U. S. Atomic Energy Commission.

(2) Department of Chemistry, University of Alabama, University, Alabama; Consultant and Summer Employee, Oak Ridge National Laboratory.

(3) Department of Physical Sciences, Arizona State College, Tempe, Arizona; Summer Participant 1954, Oak Ridge National Laboratory.

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crystallographic axes. Two independent investigators[14] agree on its crystal structure. The molybdenum atoms are arranged in a distorted cubic close-packed array with octahedrally disubstituted oxygen neighbors at varying distances. The structure is a layer lattice with oxygen atoms lying in isolated layers parallel to the 010 plane.

The low temperature heat capacity of molybdenum disulfide has been investigated previously by Anderson[15] but only above 56°K. Since this work was started Westrum and McBride[6] presented their studies of MoS_2. A prior study of molybdenum trioxide has been published by Seltz, Dunkerley and DeWitt[16] between 70°K. and room temperature. Accordingly the available data for both compounds when this work was undertaken were of insufficient range for a good test of T^2 behavior in the range below 60°K.

Experimental

Materials.—A sample of purified molybdenum disulfide (designated Grade 3) was donated for the purpose of these studies by the Climax Molybdenum Company.[17] It contained some free carbon and a trace of oil. It was purified further by extractions to remove oil and other foreign material soluble in organic solvents. The method was similar to that described by Ballou and Ross.[18] J. T. Baker Chemical Company C.P. molybdenum trioxide was used without further purification.

Apparatus and Methods.—The low temperature adiabatic calorimeter and cryostat have been described previously.[5,12] The calorie equal to 4.1840 absolute joules was used to convert from electrical to thermal energy units. The temperature scale was established with a calorimetric-type platinum resistance thermometer calibrated from 10°K. to 500°C. by the National Bureau of Standards. This thermometer was also checked by us at the ice point using our regular Mueller bridge.

The calorimeter can, including thermometer and heater, weighed 54.473 g. and was calibrated according to our previous procedure. The sample of molybdenum disulfide weighed 97.234 g. (0.6074 mole), the molybdenum trioxide 87.385 g. (0.6070 mole). The formula weights of molybdenum disulfide and molybdenum trioxide were taken as 160.08 and 143.95, respectively (1952 atomic weights). All weights have been corrected to vacuum. In each case 3 to 5 mm. of dry helium at room temperature was admitted to the can after carefully evacuating the samples. The overall accuracy of the C_p measurements is about 0.2% above 50°K. and perhaps 0.5% at 20°K.

Results and Discussion

Our major interest in this investigation was to learn whether molybdenum trioxide and molybdenum disulfide show a T^2 heat capacity dependence in the range below 60°K. Therefore, in view of the published work of others,[6,15,16] we carried our measurements above about 80°K. to learn whether our results agreed with prior publications. The agreement was good in the case of molybdenum disulfide. However, our results for molybdenum trioxide show a systematic difference over most of the temperature range from the results of Seltz, Dunkerley and DeWitt.[16] There is a discrepancy in the paper of Seltz, Dunkerley and DeWitt[16] between the sample weight in grams and the derived number of moles of MoO_3. Correspondence with one of the authors has not resolved the inconsistency. Accordingly we are reporting our results for the entire temperature range for molybdenum trioxide, but only for the lower temperature range for molybdenum disulfide.

The raw heat capacity (C_p) data for one mole of molybdenum trioxide and molybdenum disulfide are given in Tables I and II, respectively. T_m is the mean temperature of an individual measurement and the approximate temperature rise can be judged from successive T_m values. The measurements were taken in the order in which they are

TABLE I

RAW DATA—HEAT CAPACITY OF MoO_3

T_m (°K.)	C_p (cal./mole deg.)	T_m (°K.)	C_p (cal./mole deg.)	T_m (°K.)	C_p (cal./mole deg.)
94.01	7.017	233.06	15.583	19.60	0.387
98.19	7.388	237.86	15.788	24.65	0.578
102.18	7.754	242.62	15.967	27.47	0.735
106.02	8.088			29.89	0.949
109.73	8.401	241.77	15.948	31.86	1.066
113.31	8.698	246.45	16.120	35.64	1.301
116.79	8.970	251.10	16.295	40.69	1.730
121.10	9.312	255.70	16.458	44.48	2.100
126.20	9.716	260.27	16.611	47.72	2.425
131.10	10.085	264.79	16.776	50.56	2.707
135.85	10.447	269.28	16.951	54.53	3.097
140.49	10.762	273.74	17.094	59.43	3.606
145.03	11.076	278.15	17.275		
149.46	11.368	282.54	17.384	18.27	0.316
153.79	11.640	286.89	17.544	20.86	0.516
158.04	11.918	291.20	17.704	23.68	0.580
162.22	12.165	295.49	17.832	30.02	0.890
167.21	12.449	299.76	17.929	36.99	1.418
172.98	12.785			41.58	1.827
178.65	13.083	55.25	3.173	45.24	2.188
		58.72	3.524	48.36	2.492
176.10	12.964	63.10	3.995	51.12	2.759
181.69	13.264	67.02	4.390	55.02	3.143
187.18	13.541	70.62	4.754		
192.58	13.826	73.97	5.074		
197.89	14.076	77.12	5.397		
203.13	14.308	80.11	5.703		
208.28	14.577	83.83	6.069		
213.38	14.778	88.54	6.527		
218.34	15.007	92.96	6.945		
223.30	15.224	97.17	7.299		
228.21	15.391	101.19	7.675		

TABLE II

RAW DATA—HEAT CAPACITY OF MoS_2

T_m (°K.)	C_p (cal./mole deg.)	T_m (°K.)	C_p (cal./mole deg.)
55.32	2.101	25.37	0.500
59.44	2.409	19.69	.179
64.56	2.817	23.55	.375
69.06	3.161	27.53	.533
74.58	3.606	30.88	.659
80.96	4.152	34.18	.823
86.68	4.669	38.63	1.042
91.99	5.142	43.71	1.317
96.94	5.561	48.58	1.645
101.54	5.965	53.43	1.880
		57.66	2.279

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[16] H. Seltz, F. J. Dunkerley and B. J. DeWitt, *ibid.*, **65**, 600 (1943).

[17] We wish to thank Mr. R. H. Maurer of the Climax Molybdenum Company of Michigan for placing this sample at our disposal.

[18] E. V. Ballou and S. Ross, *J. Phys. Chem.*, **57**, 653 (1953).

recorded, the breaks in the tables indicating new series of measurements. Smoothed molar thermodynamic functions of molybdenum trioxide are listed at 10° intervals between 10 and 300°K. in Table III and the corresponding values for molybdenum disulfide up to 100°K. in Table IV. The values were obtained by standard graphical methods from large scale plots.

TABLE III

SMOOTHED THERMODYNAMIC FUNCTIONS FOR MoO_3

T (°K.)	C_p (cal./mole deg.)	S^0 (cal./mole)	$\frac{-(F^0 - H^0_0)}{T}$ (cal./mole deg.)	$\frac{(H^0 - H^0_0)}{T}$ (cal./mole deg.)
10		0.048	0.025	0.023
20	0.39	.197	.073	.124
30	0.90	.450	.153	.297
40	1.67	.811	.271	.540
50	2.65	1.286	.416	.870
60	3.66	1.857	.608	1.249
70	4.69	2.499	.832	1.667
80	5.68	3.189	1.083	2.106
90	6.66	3.916	1.358	2.558
100	7.56	4.665	1.652	3.013
110	8.42	5.427	1.960	3.467
120	9.23	6.195	2.281	3.914
130	10.00	6.965	2.612	4.353
140	10.73	7.733	2.950	4.783
150	11.40	8.497	3.294	5.203
160	12.02	9.253	3.643	5.610
170	12.61	10.000	3.995	6.005
180	13.17	10.737	4.350	6.387
190	13.69	11.463	4.705	6.758
200	14.18	12.178	5.062	7.116
210	14.64	12.881	5.418	7.463
220	15.07	13.572	5.773	7.799
230	15.48	14.251	6.127	8.124
240	15.87	14.919	6.480	8.439
250	16.25	15.574	6.831	8.743
260	16.61	16.219	7.180	9.039
270	16.96	16.853	7.526	9.327
273.15	17.07	17.050	7.635	9.415
280	17.30	17.476	7.870	9.606
290	17.65	18.090	8.212	9.878
298.15	17.93	18.580	8.489	10.091
300	17.98	18.695	8.551	10.144

TABLE IV

SMOOTHED MOLAR THERMODYNAMIC FUNCTIONS FOR MoS_2

T (°K.)	C_p (cal./mole deg.)	S^0 (cal./mole)	$\frac{-(F^0 - H^0_0)}{T}$ (cal./mole deg.)	$\frac{(H^0 - H^0_0)}{T}$ (cal./mole deg.)
20	0.28	0.140	0.055	0.085
30	0.63	.315	.110	.205
40	1.12	.56	.19	.37
50	1.74	.87	.29	.58
60	2.46	1.25	.42	.83
70	3.24	1.69	.57	1.12
80	4.07	2.17	.74	1.43
90	4.97	2.71	.93	1.78

Log-log plots of C_p *vs.* T have been made for both compounds over the entire temperature range. In the case of molybdenum disulfide the plot is practically linear from 19.7° to 65°K. and has a slope of 2.0, while the corresponding range of molybdenum trioxide gives an essentially linear plot in which the slope is about 2.1. Above 60°K. the curves fall off smoothly to a slope of less than 0.5 at room temperature. This shows that the heat capacity of these two compounds follows a nearly T^2 dependence in the range from 20 to 60°K.; the agreement is comparable with that found by several of us for boron nitride.[5] In the case of molybdenum disulfide Westrum and McBride[6] noted a temperature dependence of C_p as near T^2 as that observed for graphite[4] and boron nitride.[5] Figure 1 is a plot of C_p against T^2 for MoS_2 and MoO_3 up to about 70 or 80°K. Reasonably straight lines are obtained consistent with approximately T^2 behavior over this range. One notes that the lines extrapolate to zero heat capacity at absolute zero within the limits of experimental error. It seems probable that below our measured temperature range the heat capacity dependence rises, probably to about T^3. However, the difference between T^2 and T^3 dependence is not large at very low temperature where the heat capacity is quite small and so the T^2 plot extrapolates to zero at 0°K.

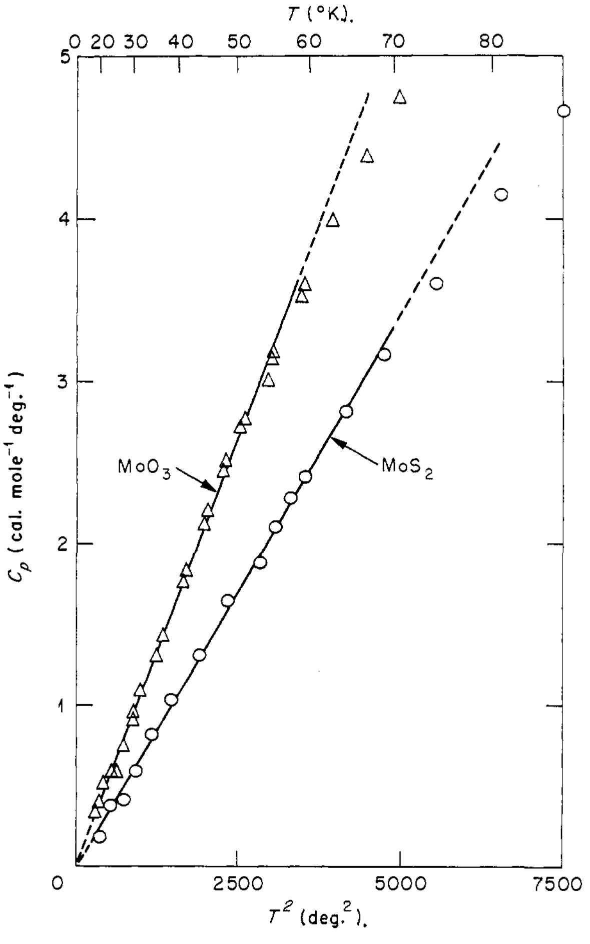

Fig. 1.—C_p *vs.* T^2 for MoO_3 and MoS_2.

The difference between an assumed T^3 heat capacity dependence and the observed approximate T^2 dependence does make appreciable difference in extrapolations from 60 or 70°K. to absolute zero. Anderson[15] calculates the entropy of MoS_2 to be

0.99 e.u. at 56.2°K., using a combined Debye–Einstein type extrapolation. Our results give a value of 1.10 e.u. at this temperature. In the case of MoO_3 the previously published data[16] showed a value of 2.966 e.u. at 70.05°K. which is to be compared with our result of 2.50 e.u. at 70°K. Using the Bureau of Standards Compilation[19] for the heat of formation of molybdenum trioxide and the entropies of molybdenum and oxygen we derive for the reaction

$$Mo(c) + 3/2O_2(g) = MoO_3(c)$$

at 298.15°K. these values: $\Delta S_f^0{}_{298.15} = -61.75$ e.u. and $\Delta F_f^0{}_{298.15} = -161.92$ kcal./mole.

It is now evident that a number of anisotropic substances fail to follow the Debye T^3 law in the range between 15 and 60°K. The low temperature heat capacity results reported here show that it is quite important for measurements to extend well below 50°K. and preferably into the helium range if one is to derive satisfactory values for the entropy. In particular, extrapolations from 50°K. in the case of heavy substances may be subject to serious error.

Oak Ridge, Tennessee

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[Contribution from the Watson Laboratory of International Business Machines]

Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. II. Phase Diagram of the System K_2CO_3–V_2O_5

By Frederic Holtzberg, Arnold Reisman, Margaret Berry and Melvin Berkenblit

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The high temperature equilibrium between V_2O_5 and K_2O or K_2CO_3 has been reinvestigated using thermal and X-ray analysis. Five compounds have been found corresponding to the formulas (I) $K_2O \cdot 4V_2O_5$, (II) $K_2O \cdot V_2O_5$, (III) $16K_2O \cdot 9V_2O_5$, (IV) $2K_2O \cdot V_2O_5$, and (V) $3K_2O \cdot V_2O_5$. II and IV melt congruently at 520 and 910°, respectively. IV undergoes an α- to β-transformation at 740°. Compounds I and III melt incongruently at 520 and 696°, respectively. Within experimental limits, I appears to occur at a singular point between congruent and incongruent melting. V melts at approximately 1300°. X-Ray powder data have been obtained for all the anhydrous compounds of this system, and are available through the A.D.I. Thermal and X-ray analysis failed to reveal the presence of previously reported allotropic modifications of V_2O_5.

Introduction

This paper is the second in a series involving the study of the high temperature reactions of K_2O and K_2CO_3 with the group VB pentoxides.[1] Many compounds having the molecular formula $(K_2O)_x \cdot (V_2O_5)_y$ have been reported in the literature. Mellor[2] abstracts the methods for the preparation of the following anhydrous potassium vanadates, with x to y ratios 4:1, 3:1, 2:1, 1:1, 1:3 and 2:9. Ephraim[3] also lists a 3:5 compound without a method of preparation. In 1928, Canneri[4] studied the reactions of the alkali oxides with V_2O_5. The results of his partial investigation of the system K_2O–V_2O_5, Fig. 1, indicated the formation of only 3 anhydrous potassium vanadates with x to y ratios 1:1, 2:1, and 3:1. Canneri also showed that the equilibrium pressure of oxygen varied with composition, exhibiting a maximum O_2 evolution at approximately 44 mole % K_2O. There was no apparent attempt to relate the results of the oxygen loss experiments to the effect it might have in the determination of the phase diagram.

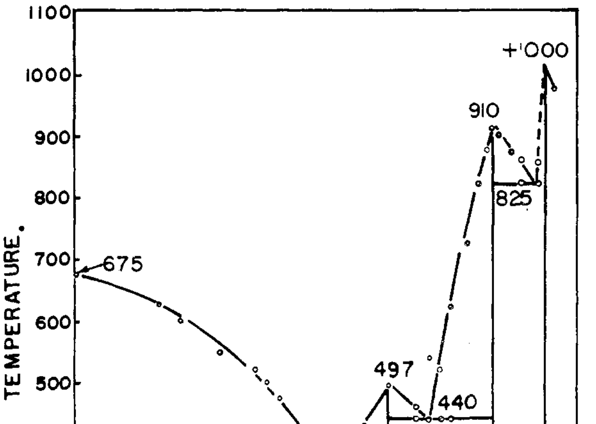

Fig. 1.—Partial phase diagram of the system K_2O–V_2O_5 reconstructed from Canneri's data.

In editorial comment both Ephraim and Mellor express some doubt as to the actual existence of all the compounds reported. It was felt that an examination of the complete phase diagram, using techniques of thermal and X-ray analysis, might help clarify the uncertainties concerning the actual number of compounds in this system.

In addition to the confused state of the V_2O_5–K_2O chemistry, the question of allotropic modifications of V_2O_5 arises. Ditte[5] reported the existence of three allotropic modifications of V_2O_5, each having different color and different water solubility. Brauer,[6] and Frevel and Rinn[7] reported on the structural modifications of the low and high temperature forms of Nb_2O_5 and Ta_2O_5. A survey of

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