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Low-temperature heat capacities of molybdenum tri- and tetrachlorides[a]

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No thermal anomalies were detected in the heat capacities of $MoCl_3$ and $MoCl_4$ determined by adiabatic calorimetry from 5 to 350 K. The heat capacity C_p(298.15 K), entropy $\{S°(298.15\ K) - S°(0)\}$, and the function $\{G°(298.15\ K) - H°(0)\}/298.15\ K$ are (for $MoCl_3$) 22.66, 28.24, and −13.85; and (for $MoCl_4$) 28.28, 37.58, and −18.62 $cal_{th}\ K^{-1}\ mol^{-1}$. The Gibbs energies of formation for these compounds at 298.15 K are −111.4 and −137.2 $kcal_{th}\ mol^{-1}$, respectively.

1. Introduction

Although the thermochemistry of the molybdenum chlorides have been investigated much more than that of the other molybdenum halides, there is still a paucity of thermophysical data. The low melting temperature and volatility of molybdenum chlorides have been employed as a means of extraction for upgrading and enriching molybdenum ores.[1] Appropriate thermal data might assist in the application and understanding of this scheme as well as in technical catalysis application.

2. Experimental

APPARATUS

Heat-capacity measurements were made in the Mark II adiabatic cryostat which has been described previously.[2] The samples were contained in a gold-plated copper calorimeter (laboratory designation W–48) which incorporates a gold gasket and screw seal, gold-plated copper vanes to enhance conductivity, has a mass of 33.47 g and an internal volume of 44.44 cm^3. The temperature of the calorimeter was measured with a capsule-type, 25 Ω (nominal) resistance, platinum-resistance thermometer (laboratory designation A-5) inserted into a reentrant well in the calorimeter and previously calibrated by the National Bureau of Standards. The

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resultant temperature scale was judged to correspond to the (IPTS 1968) temperature scale to within 0.03 K from 10 to 90 K and within 0.04 K from 90 to 350 K. A 150 Ω constantan heater, wound non-inductively on a cylindrical gold-plated copper heater-core surrounds the resistance thermometer.

SAMPLE PROCUREMENT AND PURITY

The samples and analytical data on them were generously supplied to us by Climax Molybdenum Company of Michigan. The brown-red α-phase molybdenum trichloride ($MoCl_3$) was found to contain 47.32 mass per cent (theoretical: 47.42) and 51.96 mass per cent chlorine (theoretical: 52.58). These analyses for the components total 99.28 per cent and yield a mole ratio $n(Cl)/n(Mo)$ of 2.97. The only contaminant found was <0.1 mass per cent of tin. Infrared absorption data revealed that the product was anhydrous and completely free of contaminating oxyhalides. The black α-phase molybdenum tetrachloride ($MoCl_4$) contained 40.45 mass per cent molybdenum (theoretical: 40.35) and 57.82 mass per cent chlorine (theoretical: 59.64). The total is 98.27 per cent and the apparent mole ratio $n(Cl)/n(Mo)$ is 3.96. Only 0.34 mass per cent of the sample proved to be insoluble in acid and 0.28 mass per cent insoluble in base. The analytical results indicate that a satisfactory mole ratio of the elements and an acceptable level of insolubles was achieved in the preparation of this sample. Infrared analyses further indicated that the sample was free of extraneous moisture and that the proper adsorption bands were present.

The samples were loaded into the calorimeter in a nitrogen-atmosphere dry box to avoid reaction in moist air, then loaded into the stainless-steel sealing vessel which was subsequently highly evacuated. To facilitate rapid thermal equilibration, small amounts of helium gas (about 70 Torr) were introduced prior to sealing.† The sealing of the calorimeter, weighing, loading in the cryostat, and the processing of the heat-capacity results have been described elsewhere.[3] Table 1 indicates the masses m

TABLE 1. $MoCl_3$ and $MoCl_4$ sample details: molar mass M, mass of sample m, density ρ, and pressure p of helium
(Torr = (101 325/760) Pa)

Compound	M/g mol^{-1}	m/g	ρ/g cm^{-3}	p(He)/Torr
$MoCl_3$	202.299	40.8257	3.75 [a]	71
$MoCl_4$	237.752	41.0462	3.19 [b]	74

[a] Reference 4.
[b] Reference 5.

of samples, molar masses M, densities ρ, and helium pressures p(He). All measurements of mass, temperature, resistance, potential, and time are referred to standardizations and calibrations by the National Bureau of Standards. Adjustment for vaporization of the sample into the gas space in the calorimeter was found to be negligible.

† Throughout this paper Torr = (101 325/760) Pa; cal_{th} = 4.184 J.

3. Results and conclusion

The experimental heat capacities of molybdenum trichloride and tetrachloride are reported in table 2 and the curves are depicted in figure 1. Figure 2 shows plots of

TABLE 2. Heat capacities of molybdenum trichloride and tetrachloride
(cal_{th} = 4.184 J)

T/K	C_p/$cal_{th}\,K^{-1}\,mol^{-1}$	T/K	C_p/$cal_{th}\,K^{-1}\,mol^{-1}$	T/K	C_p/$cal_{th}\,K^{-1}\,mol^{-1}$
		Molybdenum trichloride ($MoCl_3$)			
Series I		250.48	21.46	9.09	0.1315
55.08	5.881	261.04	21.74	9.99	0.1750
59.75	6.630	271.80	22.01	11.21	0.2382
66.66	7.705			12.52	0.3166
75.11	8.921	Series II		13.71	0.3987
83.54	10.16	255.61	21.61	15.09	0.5006
91.80	11.24	265.98	21.86	16.73	0.6234
100.32	12.28	276.61	22.12	18.52	0.7693
109.50	13.30	287.49	22.36	20.39	0.9466
120.06	14.42	298.27	22.62	22.54	1.165
131.34	15.50	309.54	22.89	25.13	1.456
142.03	16.40	321.27	23.23 [a]	27.65	1.767
152.60	17.16	332.94	23.50 [a]	30.18	2.100
163.43	17.86	344.55	23.63 [a]	33.76	2.608
174.23	18.46			37.68	3.183
185.03	18.99	Series III		41.40	3.726
195.87	19.49	4.91	0.0221	46.22	4.475
206.86	19.92	5.66	0.0238	51.42	5.315
218.00	20.37	6.62	0.0415	55.96	6.024
228.97	20.76	7.49	0.0678	61.40	6.891
239.79	21.12	8.26	0.0937	68.84	8.018
		Molybdenum tetrachloride ($MoCl_4$)			
Series I		250.69	26.89	9.415	0.3078
53.69	8.226	261.70	27.22	10.50	0.4134
59.58	9.391	272.96	27.55	11.62	0.5397
67.16	10.83			12.93	0.6930
74.85	12.16	Series II		14.38	0.8861
82.99	13.59	258.59	27.12	15.93	1.105
92.62	15.09	269.56	27.46	17.54	1.345
102.76	16.48	280.44	27.73	19.19	1.601
112.51	17.75	291.20	28.05	20.83	1.880
121.96	18.90	302.26	28.32	22.50	2.159
131.89	20.00	313.86	28.58	24.66	2.552
142.33	21.01	325.67	28.88	27.19	3.017
152.98	21.93	337.44	29.00	27.35	3.046
163.89	22.74	348.80	29.07	30.27	3.600
174.79	23.47			34.08	4.345
185.41	24.08	Series III		38.18	5.144
196.12	24.65	4.808	0.0499	42.48	5.972
206.94	25.16	5.421	0.0624	47.24	6.947
217.86	25.68	6.237	0.0912	52.41	7.978
228.95	26.12	7.169	0.1382	58.60	9.196
239.91	26.53	8.283	0.2139	65.05	10.45

[a] Not included in curve fit.

C_p/T against T^2 for extrapolation of each set of results to $T = 0$. The smoothed thermodynamic functions for each compound at selected temperatures are reported in tables 3 and 4, respectively. These data have been adjusted for curvature and are given in terms of the IPTS–68 and molar masses (given in table 1) calculated from

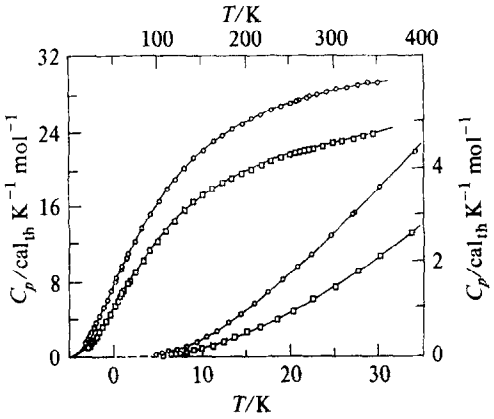

FIGURE 1. Heat capacities of molybdenum trichloride --□-- and molybdenum tetrachloride --○--.

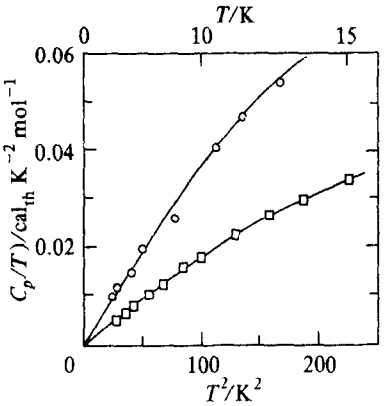

FIGURE 2. C_p/T plotted against T^2 for molybdenum trichloride --□-- and tetrachloride --○--.

the 1968 atomic weights. The probable errors of the heat-capacity measurements are considered to be 0.2 per cent above 25 K, but increase gradually to 5 to 10 per cent at 5 K. Heat capacities at selected temperatures listed in tables 3 and 4 were taken from a smooth curve obtained by a least-squares fitted polynomial through experimental points and extrapolated below 5 K by use of figure 2. Thermodynamic functions given in these tables were obtained by integrating the thermal data using a high-speed computer. They are considered to have a probable error of about

TABLE 3. Thermodynamic functions of molybdenum trichloride
(cal_{th} = 4.184 J)

T / K	C_p / $cal_{th}\,K^{-1}\,mol^{-1}$	$S°(T) - S°(0)$ / $cal_{th}\,K^{-1}\,mol^{-1}$	$H°(T) - H°(0)$ / $cal_{th}\,mol^{-1}$	$-\{G°(T) - H°(0)\}/T$ / $cal_{th}\,K^{-1}\,mol^{-1}$
5	0.0218	0.0072	0.0261	0.0020
10	0.175	0.0545	0.411	0.0135
15	0.492	0.182	2.035	0.0463
20	0.907	0.378	5.486	0.103
25	1.440	0.635	11.300	0.183
30	2.081	0.953	20.066	0.284
35	2.784	1.326	32.213	0.406
40	3.520	1.745	47.960	0.546
45	4.287	2.204	67.463	0.705
50	5.080	2.698	90.920	0.879
60	6.661	3.764	149.64	1.270
70	8.198	4.907	223.99	1.707
80	9.652	6.097	313.31	2.181
90	11.00	7.313	416.69	2.684
100	12.25	8.538	533.05	3.208
110	13.39	9.760	661.32	3.748
120	14.42	10.97	800.45	4.299
130	15.36	12.16	949.41	4.859
140	16.20	13.33	1107.3	5.422
150	16.96	14.48	1273.1	5.988
160	17.64	15.59	1446.2	6.553
170	18.24	16.68	1625.6	7.117
180	18.78	17.74	1810.8	7.678
190	19.26	18.77	2001.0	8.234
200	19.69	19.77	2195.8	8.786
210	20.08	20.74	2394.7	9.332
220	20.44	21.68	2597.4	9.872
230	20.77	22.59	2803.4	10.405
240	21.09	23.49	3012.8	10.932
250	21.40	24.35	3225.2	11.451
260	21.69	25.20	3440.7	11.964
270	21.97	26.02	3659.0	12.469
280	22.24	26.83	3880.1	12.968
290	22.48	27.61	4103.7	13.459
300	22.70	28.38	4329.7	13.944
310	22.90	29.12	4557.7	14.421
320	23.07	29.85	4787.5	14.892
330	23.27	30.57	5019.2	15.356
340	23.54	31.26	5253.1	15.814
350	23.99	31.95	5490.5	16.265
273.15	22.06	26.28	3728.3	12.627
298.15	22.66	28.24	4287.7	13.855

TABLE 4. Thermodynamic functions of molybdenum tetrachloride
(cal_{th} = 4.184 J)

T / K	C_p / $cal_{th}\ K^{-1}\ mol^{-1}$	$S°(T) - S°(0)$ / $cal_{th}\ K^{-1}\ mol^{-1}$	$H°(T) - H°(0)$ / $cal_{th}\ mol^{-1}$	$-\{G°(T) - H°(0)\}/T$ / $cal_{th}\ K^{-1}\ mol^{-1}$
5	0.0530	0.0176	0.0661	0.0044
10	0.364	0.127	0.943	0.0327
15	0.971	0.382	4.194	0.103
20	1.738	0.764	10.915	0.218
25	2.609	1.244	21.747	0.374
30	3.550	1.802	37.125	0.564
35	4.523	2.422	57.300	0.785
40	5.501	3.090	82.358	1.031
45	6.497	3.795	112.35	1.298
50	7.498	4.531	147.33	1.585
60	9.468	6.073	232.22	2.203
70	11.34	7.675	336.36	2.870
80	13.08	9.305	458.58	3.572
90	14.68	10.94	597.51	4.300
100	16.14	12.56	751.70	5.045
110	17.46	14.16	919.81	5.802
120	18.67	15.74	1100.6	6.564
130	19.76	17.27	1292.8	7.329
140	20.75	18.77	1495.4	8.093
150	21.65	20.24	1707.5	8.854
160	22.46	21.66	1928.1	9.610
170	23.18	23.04	2156.4	10.360
180	23.82	24.39	2391.4	11.102
190	24.39	25.69	2632.5	11.836
200	24.89	26.96	2879.0	12.560
210	25.34	28.18	3130.2	13.275
220	25.75	29.37	3385.7	13.980
230	26.12	30.52	3645.1	14.674
240	26.48	31.64	3908.1	15.358
250	26.81	32.73	4174.6	16.031
260	27.14	33.79	4444.3	16.694
270	27.46	34.82	4717.4	17.346
280	27.78	35.82	4993.6	17.988
290	28.07	36.80	5272.8	18.620
300	28.32	37.76	5554.8	19.242
310	28.54	38.69	5839.1	19.855
320	28.71	39.60	6125.4	20.458
330	28.84	40.49	6413.2	21.051
340	28.98	41.35	6702.3	21.635
350	29.19	42.19	6993.0	22.211
273.15	27.56	35.14	4804.1	17.550
298.15	28.28	37.58	5502.4	19.128

0.1 per cent above 100 K. However, it should be noted that they have been extrapolated to $T = 0$ on the basis of figure 2. This procedure, of course, neglects possible magnetic ordering and other effects between the lowest temperature of measurement (5 K) and absolute zero.

From the results of the calorimetrically determined $S°$'s at 298.15 K in this research, together with $S°(Cl_2, g, 298.15\ K) = 53.29\ cal_{th}\ K^{-1}\ mol^{-1}$,[6] and Shchukarev *et al.*'s[7] $\Delta H_f°$ for $MoCl_3(c)$ and $MoCl_4(c)$, a $\Delta G_f°(298.15\ K)$ of $15.44\ kcal_{th}\ mol^{-1}$ was computed for the reaction $MoCl_4(c) = MoCl_3(c) + \frac{1}{2}Cl_2(g)$. This accords well with a statement in the literature[7] that the reaction does not readily take place as written.

These data together with the entropy of molybdenum[8] lead to the values of $\Delta H_f°$, $\Delta S_f°$, and $\Delta G_f°$'s presented in table 5.

TABLE 5. Thermodynamics of formation for $MoCl_3(c)$ and $MoCl_4(c)$ at 298.15 K ($cal_{th} = 4.184$ J)

Compound	$-\Delta G_f°$ / $kcal_{th}\ mol^{-1}$	$-\Delta H_f°$ / $kcal_{th}\ mol^{-1}$	$\Delta S_f°$ / $cal_{th}\ K^{-1}\ mol^{-1}$
$MoCl_3(c)$	111.4 ± 2	94.0 ± 2	58.32 ± 0.03
$MoCl_4(c)$	137.2 ± 2	114.6 ± 2	75.34 ± 0.04

Supplementary material concerning the physical properties of the chlorides studied, together with a survey of the magnetic behavior as it affects thermodynamics, as well as numerous standard Gibbs energies of reaction involving these and related substances are presented elsewhere.[9]

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REFERENCES

1. Zelikhan, A. N.; Stefanyuk, S. L.; Ch'ang, Ch'ih, Luang; Leonov, L. M. *Izv. Vyssh. Ucheb. Zaved. Tsvet. Met.* **1970,** 13, 78.
2. Westrum, E. F., Jr.; Furukawa, G. T.; McCullough, J. P. "Adiabatic low-temperature calorimetry". In *Experimental Thermodynamics*, Vol. 1, McCullough, J. P.; Scott, D. W.: editors. Butterworths: London. **1968.**
3. Kiwia, H. L.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1975,** in press.
4. Schnering, H-G.; Wöhrle, H. *Naturwissenschaften* **1963,** 50. 91.
5. Schäfer, H.; Schnering, H-G.; Tillack, J.; Kuhnen, F.; Wöhrle, H.; Bauman, H. *Z. Anorg. Allgem. Chem.* **1967,** 353, 281.
6. Shchukarev, S. A.; Vasil'kova, I. V.; Sharupin, B. N. *J. Gen. Chem. USSR* **1956,** 26, 2335.
7. Shchukarev, S. A.; Novikov, G. I.; Vasil'kova, I. V.; Suvorov, A. V.; Andreeva, N. V.; Sharupin, B. N.; Baev, A. K. *Russ. J. Inorg. Chem.* **1960,** 5, 802.
8. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumme, R. H. *Natl. Bur. Stand.* (U.S.) Tech. Notes No. 270-4. U.S. Govt. Printing Office: Washington, D.C. **1969.**

9. For supplementary material including adjuvant, structural, and physical properties of the substances reported in this paper and derived thermodynamics of chemical reactions made possible by the new data, order NAPS document No. 02546 for 45 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number. Make checks payable to Microfiche Publications. Photocopies are $7.25. Microfiche are $1.50. Outside of the U.S. or Canada, postage is $2.00 for a photocopy or $0.50 for a fiche.