289. *Comparison of Calorimetric and Spectroscopic Entropies of Molybdenum Hexacarbonyl.*

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The heat of sublimation of molybdenum hexacarbonyl at 90° has been measured and is 16·66 kcal./mole. By combining this with data in the literature, the calorimetrically determined standard entropy of the gas at 25° is calculated to be 118·0 cal. mole^{-1} deg.$^{-1}$. This is compared with entropies calculated from three different vibrational assignments in the literature and it is concluded that one of these assignments fails to give an entropy in satisfactory accord with the calorimetric value.

An attempt is now being made in this laboratory to obtain additional experimental data on the vibrational spectra of the Group VI metal carbonyls, $M(CO)_6$ (M = Cr, Mo, W), in order to make possible a more certain assignment of the fundamental vibrational frequencies in these molecules. Hawkins, Mattraw, Sabol, and Carpenter [1] have reported fairly complete infrared spectra. However, the number of infrared-active fundamentals observed was only three, so the frequencies they propose for all 13 fundamentals are naturally somewhat uncertain, being based on extensive and unavoidably risky deductions from the combination bands observed. Using their assignments and the published molecular structure parameters,[2] they calculated the standard entropy of the gas at 298° K to be 121·07 cal. mole^{-1} deg.$^{-1}$. Murata and Kawai [3] applied a Urey–Bradley force field in order to compute force constants from the data of Hawkins *et al.*[1] They were led to reassign ν_{10} and ν_{12} from 230 and 327 cm.$^{-1}$, respectively, to 557 and 517 cm.$^{-1}$. They did not recalculate thermodynamic functions. Most recently, Danti and Cotton [4] have studied the Raman spectrum and find ν_{11} at 62·4 cm.$^{-1}$ rather than at 80 cm.$^{-1}$ as estimated by Hawkins *et al.*[1] The three sets of assignments will hereafter be denoted HMSC,[1] MK,[3] and MK-DC.[4]

We have measured the heat of sublimation of molybdenum hexacarbonyl in the range 70—110° by determining the temperature dependence of the vapour pressure. Just as with other metal carbonyls we have studied, the rate of decomposition to metal and carbon monoxide in the temperature range where the vapour pressures are appreciable is fairly rapid and it is necessary to make corrections for the pressure of the carbon monoxide produced. The apparatus used and the procedure, which permits making

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[1] Hawkins, Mattraw, Sabol, and Carpenter, *J. Chem. Phys.*, 1955, **23**, 2422.
[2] Brockway, Ewens, and Lister, *Trans. Faraday Soc.*, 1938, **34**, 1350.
[3] Murata and Kawai, *J. Chem. Phys.*, 1957, **27**, 605.
[4] Danti and Cotton, *J. Chem. Phys.*, 1958, **28**, 736.

these corrections, have been described already.[5] Our data fit the equation $\log_{10} = 11{\cdot}174 - 3561{\cdot}3/T$, giving a value of 16·66 kcal./mole for the enthalpy of sublimation at 363° K. Two previous determinations of this quantity have been reported.[6,7] Hieber and Romberg [6] measured vapour pressures in a temperature range slightly higher than ours. They observed that decomposition occurred and therefore worked quickly to minimize its effect. They proposed a value of 16·29 kcal./mole for the enthalpy of sublimation. Lander and Germer [7] measured vapour pressures at 18·5°, 28·1°, and 35·2° by the vapour saturation method and proposed a value of 17·39 kcal./mole for the enthalpy of sublimation. They also suggested that Hieber and Romberg had not put the best line through their data and they proposed another line, the slope of which gives a ΔH of sublimation of 16·72 kcal./mole. It appears to us that the latter value is indeed a more reasonable one to infer than the one which Hieber and Romberg themselves inferred, but in view of the dubious procedure employed to deal with the problem of decomposition we did not feel that the data themselves merited confidence. Also, Lander and Germer's data, only three points over a small temperature range, did not appear adequate to provide an enthalpy of high reliability. Actually, Hieber and Romberg's data do yield a result in rather good agreement with ours, and, after correction for the difference in temperature ranges (see below), so do the data of Lander and Germer.

In order to calculate the standard entropy of gaseous molybdenum hexacarbonyl at 25° from calorimetric data, the following procedure was employed. From the heat capacity data of Astrov, Itskevitch and Sharifov,[8] the enthalpy of equation (1) was estimated by extrapolation:

$$\mathrm{Mo(CO)_6(s,\ 298{\cdot}16^\circ) = Mo(CO)_6(s,\ 363{\cdot}16^\circ)};\ \Delta H = 3966\ \mathrm{cal./mole} \quad . \quad . \quad (1)$$

The heat capacity of the gas was calculated by using the MK-DC vibrational assignments, and the enthalpy of equation (2) calculated:

$$\mathrm{Mo(CO)_6(g,\ 363{\cdot}16^\circ) = Mo(CO)_6(g,\ 298{\cdot}16^\circ)};\ \Delta H = -3314\ \mathrm{cal./mole} \quad . \quad (2)$$

The MK-DC assignment was used since it appears to be the most reliable, but the effect of using either of the others would only amount to about 0·1 e.u. in the final result. Combining (1), (2), and 16,660 cal./mole for ΔH of sublimation at 363·16° K, we obtain for ΔH of sublimation at 298·16° a value of 17·31 kcal./mole. Upon dividing by 298·16° we obtain 58·06 cal. mole^{-1} deg.$^{-1}$ as the entropy of process (3):

$$\mathrm{Mo(CO)_6(s,\ 298{\cdot}16^\circ) = Mo(CO)_6(g,\ 298{\cdot}16^\circ,\ 7{\cdot}767 \times 10^{-2}\ mm.)} \quad . \quad . \quad . \quad (3)$$

The equilibrium pressure at 25°, $7{\cdot}767 \times 10^{-2}$ mm., is calculated from a Clapeyron equation by using a value of ΔH of sublimation which is the average of the values at 363° and 298° K., *viz.*, 17·00 kcal./mole. This is equivalent to assuming that ΔH of sublimation varies linearly with temperature between 25° and 90°, which seems a fair assumption. For the entropy of compression at 25°, calculated by using the ideal-gas law, we obtain $-18{\cdot}26$ cal. mole^{-1} deg.$^{-1}$. Astrov *et al.*[8] give $78{\cdot}17 \pm 0{\cdot}25$ cal. mole^{-1} deg.$^{-1}$ as the entropy of the solid at 298·16° K. We therefore calculate the standard calorimetric entropy at 25° to be $78{\cdot}17 + 58{\cdot}06 - 18{\cdot}26$, or 118·0 cal. mole^{-1} deg.$^{-1}$.

This value of the entropy may now be compared with spectroscopically derived values by using the three vibrational assignments. We have used the Sackur–Tetrode equation for the translational contribution, and the tables of Miller, West, and Bernstein [9] to evaluate the vibrational contributions from the frequencies of the normal modes. For the rotational contribution we have used the accurate molecular parameters of Schomaker and Nazarian,[10]

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[5] Cotton and Monchamp, *J.*, in the press.

[6] Hieber and Romberg, *Z. anorg. Chem.*, 1935, **221**, 332.

[7] Lander and Germer, *Metals Technology*, 1947, **14**, No. 6.

[8] Astrov, Itskevitch, and Sharifov, *Zhur. fiz. Khim.*, 1955, **29**, 424.

[9] Miller, West, and Bernstein, NRC Bull. No. 1, Nat. Res. Council, Ottawa, 1951.

[10] Nazarian, Ph.D. Thesis, California Institute of Technology, 1957; personal communication from Verner Schomaker.

viz., r(Mo–C) = 2·061 ± 0·02 Å and r(Mo–O) = 3·185 ± 0·035 Å, rather than the older data in ref. 2. The newer data give S° (rot) = 25·41 ± 0·07 cal. mole^{-1} deg.$^{-1}$ whereas the older parameters gave 25·48 ± 0·16 cal. mole^{-1} deg.$^{-1}$. The results obtained are given in the Table. It can be seen that the calorimetric value lies within 1·0 unit of the spectroscopic values obtained from either the MK or the MK-DC assignments. This certainly constitutes agreement within the limits of error. Whether or not a difference of 4·6 units is within the limits of error is difficult to say with certainty, but we are inclined to think that it is not quite, since the error in the calorimetric entropy is not likely to exceed about 3·5 units. This would suggest that, so far as the entropy criterion is concerned, the reassignments made by Murata and Kawai are acceptable and also that made by Danti and Cotton.

Spectroscopic entropies from various vibrational assignments for $Mo(CO)_6$ (in cal. mole^{-1} deg.$^{-1}$).

	Translational contribution	Rotational contribution	Vibrational contribution	Total
HMSC	42·62	25·41 [a]	54·56	122·6
MK	42·62	25·41 [a]	49·54	117·6
MK-DC	42·62	25·41 [a]	51·04	119·1
Calorimetric value	—	—	—	118·0

[a] An uncertainty of ±0·07 is estimated from the reported uncertainties in the molecular parameters. [b] HMSC[1] give 121·1; we cannot account for the difference between our result and theirs.

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