[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Vapor Pressures of Inorganic Substances. VIII. Molybdenum between 2151 and 2462°K.[1]

BY JAMES W. EDWARDS, HERRICK L. JOHNSTON AND PAUL E. BLACKBURN

The vapor pressure of molybdenum has been determined by the vacuum evaporation method. Values have been calculated for the heat of sublimation at absolute zero and equations have been formulated for vapor pressure as a function of temperature.

Experimental Method

Apparatus and Procedure.—The vapor pressure of molybdenum has been determined at this Laboratory by the method of vacuum evaporation. The techniques and apparatus used are essentially similar to those described in earlier papers from the General Electric Research Laboratory and from this Laboratory.[2-7] Some runs were made in a glass apparatus, and others, at higher temperatures, were made in a new metal apparatus. The procedure for the glass apparatus was the same as that described in a previous paper.[7]

The metal apparatus was designed to have the following features: (1) a compact system of small volume with large connecting tubes and two-stage vacuum pumps to give high pumping speed to low ultimate pressures (10^{-7} to 10^{-8} mm.); (2) an internal resistance heater for baking out during evacuation; (3) double o-ring seals and separate evacuation of the space between the o-rings so that they would not need grease, which might contaminate the samples; and (4) a liquid air trap to prevent pump oils from backing up into the system.

Sample.—The molybdenum was a very pure sample, in the form of a solid cylinder 0.86 in. high and 0.99 in. in diameter, obtained from the Climax Molybdenum Company. A black body hole, 0.030 in. in diameter and 0.5 in. deep, was drilled into it near the edge.

The analysis furnished by the Climax Molybdenum Company showed the presence of 0.023% C. The other principal impurities, revealed by spectroscopic analysis[8] were Fe (0.01% to 0.001%) and Si (0.01% to 0.001%).

Calculations.—Vapor pressures and the heat of sublimation were calculated as previously described.[4] The area of the sample at high temperature was computed by the use of Worthing's equation[9]

$$L_{\mathrm{T}} = L_{300}[(5 \times 10^{-6})(T - 300)10.5 \times 10^{-10}(T - 300)^2]$$

for the linear thermal expansion of molybdenum. Free energy functions for the solid and gaseous states were calculated[10] from the data of Jaeger and Veenstra[11] and of C. E. Moore.[12]

Experimental Results.—The data are presented in Tables I and II and are plotted in Fig. 1. Numbers prefixed by the letter G refer to runs made in the glass apparatus, and those prefixed by the letter M refer to runs made in the metal apparatus. Run M-1 was not given any weight in the computation of the average ΔH_0^0, since the pressure in the metal system during this run was much

TABLE I

THE VAPOR PRESSURE OF MOLYBDENUM

Run No.	Temp., °K.	Effective time, sec.	Effective area cm.^{2}	Weight loss, g.	Evapn. rate, g. cm.$^{-2}$ sec.$^{-1}$ $\times 10^{-8}$	Pressure, atm. $\times 10^{-9}$
G-2	2151	24337	25.64	0.02585	4.142	4.424
G-3	2185	23439	25.60	.04182	6.971	7.504
G-5	2231	6761	25.57	.02329	13.47	15.06
G-4	2240	12092	25.66	.05051	16.28	17.75
M-4	2260	4699	25.31	.02267	19.06	20.87
G-6	2300	7716	25.79	.06589	33.11	37.60
M-1	2397	3721	25.20	.12029	128.3	144.6
M-3	2438	3937	25.14	.19297	195.0	221.7
M-2	2462	3426	25.12	.21859	254.0	290.3

TABLE II

THERMODYNAMIC CALCULATIONS FOR MOLYBDENUM

Run No.	Temperature, °K.	$-R \ln P$, cal. mole^{-1} deg.$^{-1}$	$\left(\frac{F^0 - H_0^0}{T}\right)_s - \left(\frac{F^0 - H_0^0}{T}\right)_g$ cal. mole^{-1} deg.$^{-1}$	ΔH_0^0, kcal. mole^{-1}
G-2	2151	38.23	34.18	155.75
G-3	2185	37.18	34.07	155.67
G-5	2231	35.79	33.92	155.53
G-4	2240	35.47	33.90	155.38
M-4	2260	35.14	33.83	155.88
G-6	2300	33.97	33.70	155.65
M-1	2397	31.30	33.37	155.00
M-3	2438	30.45	33.24	155.27
M-2	2462	29.91	33.15	155.26
	Average ΔH_0^0 (Run M-1 not included)			155.55
	Mean deviation			0.19

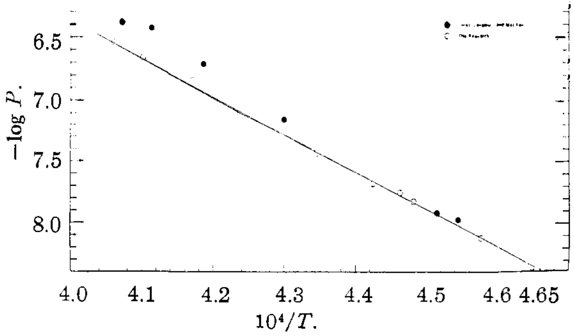

Fig. 1.—Vapor pressure of molybdenum: ●, Jones, Langmuir and MacKay; O, this research.

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[1] This work was carried out under contract between the Office of Naval Research and The Ohio State University Research Foundation.

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[8] The authors wish to express their appreciation to Mr. John Center, Chief Analyst, Battelle Memorial Institute, Columbus, Ohio, for carrying out this analysis.

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higher than in the other runs. The curve in Fig. 1 was drawn from the equation

$$R \ln P = \frac{-155550}{T} - 3.452 \times 10^{-3}\, T + 41.60 \quad (1)$$

The coefficient of the term in $1/T$ is ΔH_0^0, and the other constants were obtained by expressing the difference in the free energy function as a linear equation in T and substituting this expression in the equation

$$R \ln P = \left(\frac{F^0 - H_0^0}{T}\right)_{\text{Solid}} - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{Vapor}} - \frac{\Delta H_0^0}{T} \quad (2)$$

Errors.—The standard deviations of the experimental variables for single observations are estimated as follows:

Temperature	±3.4°
Time	±5 sec.
Weight loss	±0.0001 g.
Sample dimensions	±0.0025 cm.[2]

Comparison with Earlier Data.—The vapor pressure of molybdenum has been previously determined by Norris and Worthing[13] and by Jones, Langmuir and MacKay.[14] Norris and Worthing gave no experimental data in their paper, so that it is difficult to evaluate their results. From their empirical equation for the rate of evaporation of a molybdenum filament, calculation of an average ΔH_0^0 yields 147.6 kcal. There is an increase with temperature in ΔH_0^0 of about 5 kcal. from 1600 to 2400°K. Jones, Langmuir and MacKay's data, taken with the free energy data calculated by Richert,[10] yield an average ΔH_0^0 of 152.8 ± 1.6 kcal., which is in better agreement with our value of 155.55 ± 0.19 kcal. Values of ΔH_0^0 calculated from their data show a trend of about 7 kcal. from 2070 to 2504°K., whereas there is no appreciable temperature trend in our data. Some of the discrepancy may be due to the pressure of residual gases in their system during bakeout; their reported maximum was 10^{-3} mm., as compared to the maximum of 5×10^{-5} mm. in our system.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE LABORATORY OF NORTHWESTERN UNIVERSITY]

Hydrogenation of Organo-tin and Lead Compounds under Pressure[1]

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Both tin tetraphenyl and lead tetraphenyl undergo hydrogenation under an initial pressure of 60 atm. and at temperatures around 200° to yield the respective metal and benzene, only traces of diphenyl occurring in the reaction mixtures; copper powder has no effect on the nature of the hydrocarbons produced. Similarly, with the tin tetraethyl and tin tetraisobutyl, reaction with hydrogen yields principally ethane and isobutane, respectively.

Although the hydrogenation of a few organo-tin and lead compounds under high temperature and pressure has been studied, there appear to be discrepancies, especially with the lead derivatives, as regards the formation of hydrocarbons and the effect of metals.

A study of the conditions involved in the hydrogenation of the tetraethyl, tetramethyl and the tetraphenyl of lead under pressure was carried out by Ipatieff, Razuvaev and Bogdanov[3]; in all cases, metallic lead deposition occurred. Although the hydrocarbons were not characterized in the tetraalkyl experiments, lead tetraphenyl produced benzene and insignificant amounts of diphenyl. It is of interest to note that a variety of hydrocarbons result from heating lead tetraethyl at 250–300° in the presence of hydrogen and ethylene.[4] Dull and Simons observed the formation of diphenyl in quantitative yield when lead tetraphenyl was decomposed in the absence of catalyst or hydrogen.[5]

According to Zartman and Adkins,[6] zinc di-*n*-butyl and magnesium diphenyl when heated in copper liners under hydrogen pressure in the presence of nickel catalyst give rise mainly to *n*-butane and benzene, respectively. However, the tetraphenyl and tetra-*p*-tolyl of lead were converted to diphenyl and 4,4′-dimethyldiphenyl, respectively; lead tetraheptyl to a lesser degree, formed *n*-tetradecane and traces of heptane at 200° and under an initial hydrogen pressure of 100 atm. A further claim that lead tetraphenyl is quite stable at this temperature and pressure in the absence of nickel, is in marked contrast to earlier findings where almost, if not complete hydrogenation, was demonstrated.[3] Furthermore, Razuvaev and Koton[7,8] mention that the addition of such metals as nickel catalyzes the formation of benzene, contrary to the results of Zartman and Adkins.

In the present investigation, the dependence of metallic tin deposition on solvent (decalin, dioxane, benzene and xylene), temperature (150–225°) and duration of heating of tin tetraphenyl was explored; Table I shows the results obtained with the compound at an initial hydrogen pressure of 60 atm. In all cases, benzene was the principal hydrocarbon produced with diphenyl occurring in only minute amounts; in no run was complete hydrogenation

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(1) Presented before the Organic Division of the American Chemical Society, Boston, Massachusetts, April, 1951.

(2) University of Illinois, College of Medicine, Chicago, Illinois.

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