

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

Vapor Pressure of Inorganic Substances. III. Chromium between 1283 and 1561 °K.¹

BY RUDOLPH SPEISER, HERRICK L. JOHNSTON AND PAUL BLACKBURN

The only available data in the literature on the vapor pressure of chromium are those of Baur and Brunner.² However, their data show a decided temperature trend in the calculated values of ΔH_0° . The vapor pressure of chromium has therefore been redetermined at this Laboratory by the Langmuir method. References to the method, and description of our own techniques, have been given in earlier papers from this Laboratory.³

Experimental

The measurements consisted of determining the rate at which a chromium surface evaporated into a vacuum. Pure chromium was prepared by vacuum fusion⁴ in an arc furnace fitted with a water-cooled copper crucible as an anode and with a tungsten electrode as a cathode. Spectroscopic analysis showed 99.7% purity of the product; the 0.3% impurity was oxygen. There was no trace of either tungsten or copper. The sample was in the form of an annular ring of approximately 2.50 cm. o. d., 1.02 cm. i. d. and 0.192 cm. thick. The sample was placed in a metal cell^{5b} after thorough outgassing and was then heated by high frequency induction under a vacuum of the order of 10^{-6} mm. The outgassing was especially important for chromium because of its strong tendency to oxidize.

Temperatures were measured under black body conditions by a Leeds and Northrup disappearing filament optical pyrometer which had been calibrated against a standard lamp furnished by the National Bureau of Standards. Pyrometer readings were reproduced to $\pm 2^{\circ}$.

Results and Discussion

Experimental results are summarized in Table I and plotted as $\log P$ vs. $1/T$ in Fig. 1. The effective internal areas of the annular rings and the

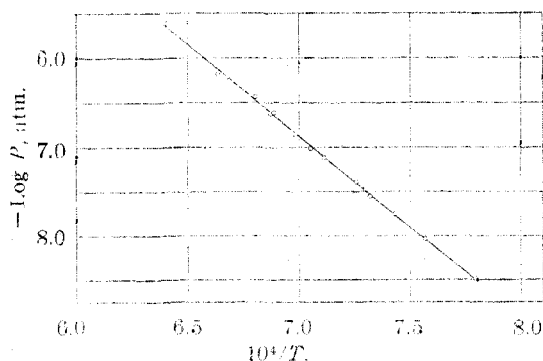


Fig. 1.—Vapor pressure of chromium.

(1) This work was supported in part by the Office of Naval Research under contract with the Ohio State University Research Foundation.

(2) E. Baur and R. Brunner, *Helv. Chim. Acta*, **17**, 958 (1934).

(3) (a) R. B. Holden, R. Speiser and H. L. Johnston, *This Journal*, **70**, 3897 (1948); (b) R. Speiser and H. L. Johnston, Preprint No. 11, Thirty-first Convention of the American Society for Metals, October 17–21, 1949, Cleveland, Ohio.

(4) D. J. MacPherson, Ph. D. Thesis, Ohio State University, 1949.

effective time at the temperature of measurement were determined as described in the first paper^{3a} of this series. The thermodynamic functions, also calculated as before, are given in Table II; the thermal data for solid and gaseous chromium were taken from the literature.⁵ The computed values of ΔH_0° , the heat of sublimation at 0°K., are constant to 93.50 kcal. to within 0.4 kcal. and show no trend with temperature.

TABLE I

VAPOR PRESSURE OF CHROMIUM

Temp., °K.	Weight loss, mg.	Eff. time, min.	Evap. rate, g./cm. ² /sec.	Pressure, atm.
1283	8.44	296.5	2.8354×10^{-8}	3.1768×10^{-9}
1321	9.22	114.2	7.9337×10^{-8}	9.0197×10^{-8}
1346	17.92	115.7	1.5338×10^{-7}	1.7602×10^{-8}
1366	13.83	56.55	2.4027×10^{-7}	2.7777×10^{-9}
1377	9.08	25.5	3.5230×10^{-7}	4.0892×10^{-8}
1405	16.19	25.4	6.3549×10^{-7}	7.4533×10^{-8}
1418	20.87	25.2	8.3057×10^{-7}	9.5097×10^{-8}
1432	29.19	25.4	1.1447×10^{-6}	1.3549×10^{-7}
1452	53.44	26.7	1.9636×10^{-6}	2.3406×10^{-7}
1455	52.72	26.9	1.9558×10^{-6}	2.3330×10^{-7}
1462	55.88	27.6	2.0152×10^{-6}	2.4103×10^{-7}
1470	72.94	23.9	3.0823×10^{-6}	3.5991×10^{-7}
1497	122.51	24.8	4.8831×10^{-6}	5.9097×10^{-7}
1507	135.83	25.5	5.3168×10^{-6}	6.4561×10^{-7}
1561	152.73	7.79	1.9252×10^{-5}	2.3793×10^{-6}

TABLE II

THERMODYNAMIC FUNCTIONS OF CHROMIUM

Run	Temp., °K.	$-\left(\frac{F^{\circ}}{RT}\right)_{\text{g}}$	$-\left(\frac{F^{\circ}}{RT}\right)_{\text{s}}$	$-\frac{R}{\log P}$	$-\log P$	ΔH_0° kcal.
1	1283	43.92	9.91	38.80	8.4980	93.53
6	1321	44.06	10.08	36.82	8.0448	93.53
3	1346	44.16	10.18	35.49	7.7545	93.51
7	1366	44.24	10.26	34.58	7.5563	93.65
2	1377	44.27	10.30	33.81	7.3884	93.06
11	1405	44.38	10.42	32.62	7.1277	93.54
8	1418	44.43	10.47	32.18	7.0318	93.79
12	1432	44.47	10.52	31.43	6.8681	93.62
5	1452	44.54	10.60	30.35	6.6306	93.35
10	1455	44.55	10.62	30.35	6.6319	93.53
9	1462	44.57	10.64	30.29	6.6180	93.89
Pre-1	1470	44.61	10.68	29.49	6.4438	93.23
1	1497	44.69	10.78	28.50	6.2284	93.43
13	1507	44.72	10.83	28.33	6.1900	93.77
4	1561	44.90	11.04	25.74	5.6236	93.04
					Mean	93.50 \pm 0.18

(5) K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, Bureau of Mines Bull. No. 383, 1935 (gaseous chromium). E. Richert, C. W. Beckett, and H. L. Johnston, *J. Techn. Report No. 102 AC 49-12-100*, Dec. 1, 1949 (solid chromium).

Our value of 93.50 kcal. for ΔH_0^0 compares with the values, 78.3 kcal., obtained by Baur and Brunner²; 80 kcal., reported by Wagman, Rossini, Evans, Levine and Joffe⁶; and 88.8 kcal., given by Kelley.⁵ The latter value is based on a single measurement at the boiling point.

Table III gives ΔH_0^0 values for the sublimation heats of the first series of transition elements. These values differ considerably from those in the table given by Seitz,⁷ which were based on older data, but still support the contention that cohesive forces are higher for metals with partially filled d shells than for those with completed d shells. Chromium fits reasonably well into the general scheme.

Least square treatment of the vapor pressure data for chromium yields the equation

$$\log P_{\text{atm}} = -(20,473/T) + 7.467$$

Summary

The vapor pressure of chromium has been measured over the temperature range 1283 to 1561°K. by determining the rate at which the metal surface evaporates into a vacuum. The ΔH_0^0 values have been calculated from the individual vapor pressure points and show no appreciable temperature trend, the average value being 93.50 ± 0.18 kcal. By combining this

(6) D. D. Wagman, F. D. Rossini, W. H. Evans, S. Levine and I. Joffe, National Bureau of Standards (1949) Series I, Table 49-1.

(7) F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 3, 427-429.

TABLE III

ΔH_0^0 VALUES FOR THE SUBLIMATION HEATS OF THE FIRST SERIES OF TRANSITION ELEMENTS

Atomic no.	Element	Electronic structure						ΔH_0^0 , kcal.
22	Ti ⁸	1s ²	2s ²	2p ⁶	3s ²	3d ²	4s ²	111.0
23	V ⁹	1s ²	2s ²	2p ⁶	3s ²	3d ³	4s ²	106.0
24	Cr	1s ²	2s ²	2p ⁶	3s ²	3d ⁵	4s ¹	93.5
25	Mn ¹²	1s ²	2s ²	2p ⁶	3s ²	3d ⁵	4s ²	...
26	Fe ¹⁰	1s ²	2s ²	2p ⁶	3s ²	3d ⁶	4s ²	96.0
27	Co ⁹	1s ²	2s ²	2p ⁶	3s ²	3d ⁷	4s ²	93.0
28	Ni ¹¹	1s ²	2s ²	2p ⁶	3s ²	3d ⁸	4s ²	101.1
29	Cu ¹⁰	1s ²	2s ²	2p ⁶	3s ²	3d ¹⁰	4s ¹	80.7
30	Zn ⁶	1s ²	2s ²	2p ⁶	3s ²	3d ¹⁰	4s ²	31.1

value of ΔH_0^0 with Kelley's free energy functions for solid and gaseous chromium, the vapor pressure equation $\log P_{\text{atm}} = -(20,434/T) + 7.415$ is obtained. Like the other transition elements of similar crystal structure with unfilled d shells, chromium has a relatively high energy of sublimation.

(8) H. J. Blocher and E. I. Campbell, THIS JOURNAL, **71**, 4040 (1949).

(9) S. Dushman, "High Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949.

(10) A. L. Marshall, R. W. Dornie and F. J. Norton, THIS JOURNAL, **59**, 1161 (1937).

(11) H. L. Johnston and A. L. Marshall, *ibid.*, **62**, 1382 (1937).

(12) The heat of sublimation of manganese is not listed here since its crystal structure is considerably different than that of the other elements in this list.

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The Compressibility of and an Equation of State for Gaseous 1-Butene

BY JAMES A. BEATTIE AND STANLEY MARPLE, JR.

In a recent paper¹ we presented measurements of the vapor pressure, orthobaric liquid volume and critical constants of 1-butene made in 1941. The same loading (6.7122 g.) of the sample was used to determine the compressibility² of 1-butene from 150 to 250°. The substance was confined in a bomb with a glass liner.²

Roper³ measured the volumetric behavior of 1-butene at low pressures from -75° to +70° from which he derived an equation for the second virial coefficient for the range -30 to +60°. Aston⁴ and co-workers computed the second virial coefficient for the temperature range -71 to -6° from measurements of vapor pressures,

(1) J. A. Beattie and S. Marple, Jr., THIS JOURNAL, **72**, 1449 (1950).

(2) For the last paper in this series see J. A. Beattie, S. Marple, Jr., and D. G. Edwards, *J. Chem. Phys.*, **18**, 127 (1950). For a description of the apparatus and method see J. A. Beattie, *Proc. Am. Acad. Arts and Sci.*, **69**, 389 (1934).

(3) E. E. Roper, *J. Phys. Chem.*, **44**, 835 (1940).

(4) J. G. Aston, H. L. Fink, A. B. Bestul, E. L. Pace and G. J. Szasz, THIS JOURNAL, **68**, 52 (1946).

heats of vaporization, and orthobaric liquid volumes. In the range -31 to -6° these values were in good agreement with those computed from Roper's equation. Olds, Sage, and Lacey⁵ measured the compressibility of 1-butene from 38 to 171° and to about 700 atmospheres.

The 1-butene used in the present investigation was furnished by the Linde Air Products Company through the courtesy of Dr. J. M. Gaines, Jr. The increase of vapor pressure with decrease in vapor volume and the slope of the isotherms in the two phase region near the critical point indicated¹ the presence of a moderate amount of impurity which did not seem to be a permanent gas.

Above 200° 1-butene polymerizes rather rapidly. As is the usual procedure we measured the pressures along each isotherm for increasing densities starting with 1 mole per liter. After the completion of the isotherm we remeasured the

(5) R. H. Olds, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **38**, 301 (1946).