The present work does not support the conclusion of Hirahara[17] that a phase transition occurs in Cu_2S at 470°.

(17) E. Hirahara, J. Phys. Soc. (Japan), 6, 422 (1951).

Chicago, Illinois

Vapor Pressures of Inorganic Substances. XI. Titanium between 1587 and 1764°K., and Copper between 1143 and 1292°K.[1]

By James W. Edwards, Herrick L. Johnston and Walter E. Ditmars

The vapor pressures of copper and titanium have been determined using the Langmuir method of vacuum evaporation. The heats of sublimation at the absolute zero have been calculated; and equations for the vapor pressure, as functions of temperature, have been formulated. The accommodation coefficients have been found to be unity. A value for the spectral emissivity for pure Ti has been found, and cooling curve data were taken which confirm McQuillan's conclusion that a sharp first-order transition from α to β occurs close to 882.5°.

Introduction

The vapor pressures of titanium and of copper have been determined in this Laboratory by the Langmuir method of vacuum evaporation. The techniques and apparatus used were identical with those described in a previous paper.[2] A check of the optical pyrometer calibration was made against a new wolfram filament lamp calibrated by the National Bureau of Standards. The new calibration was in agreement with the temperature scale in use in this Laboratory.

Materials

Titanium.—The titanium was obtained from Prof. M. G. Fontana of the Metallurgy Department of The Ohio State University, and was made by the iodide method.[3]
A spectrographic analysis[4] showed the following percentages of impurity.

Fe	0.01	Cu	0.02
Si	.03	Mo	.01
Al	.005	Sn	.005
Ca	< .01	Mn	.005
Mg	.02	Cr	.001
Ag	Not detcd.	Ti	By diff., 99.884

The sample was shaped in the form of a solid cylinder 2.9934 cm. high and 1.3398 cm. in diameter. A black body hole 0.099 cm. in diameter and about 1.52 cm. deep, was drilled near the edge of the sample for temperature measurements.
Copper.—The copper sample was made from OFHC material obtained from the American Brass Company of Waterbury, Conn. A spectrographic analysis of the sample showed the following percentages of impurity.

Fe	0.0001 to 0.001	Mo	Not detcd.	
Si	.001 to .01	Sn	Not detcd.	
Al	.001 to .01	Mn	Not detcd.	
Ca	.0001 to .001	Ca	Not detcd.	
Mg	.0001 to .001	Cu	By diff., 99.977	
Ag	.00005 to .0005			

(2) J. W. Edwards, W. E. Ditmars and H. L. Johnston, This Journal, 73, 4729 (1951).

(3) A. E. Van Arkel and J. H. de Boer, Z. anorg. allgem. Chem., 148, 345 (1925).

(4) The authors are indebted to Mr. Center, Chief Analyst, Battelle Memorial Institute, for the analysis.

The sample was in the form of a hollow closed cylinder 3.1877 cm. in height, 2.3698 cm. in diameter. The wall thickness was about 0.32 cm., while a 0.32 cm. thick plug of the sample material was press-fitted into the bore hole. There were two black body holes 0.099 cm. in diameter, one bored to a depth of 1.78 cm. near the edge, and the other bored directly into the cavity of the cylinder. The opening into the cell was used for the temperature measurement. Ordinarily, as with titanium, a cavity 1.78 cm. deep by 0.099 cm. diameter would give a nearly perfect black body, but the emissivity of copper is so low that apparent temperatures of the 1.78 cm. deep hole were 5 to 7° lower than in the central "hohlraum." No temperature gradients were observed on the sample during heating.
Both samples were suspended by means of 0.052 cm. tantalum wire.

Data and Thermodynamic Treatment

Calculations.—The calculations of the vapor pressure were made according to methods previously described.[2] The free energy functions for the solid state were calculated from data given by Kelley.[5] The high temperature values for titanium were obtained by extrapolation using the value $C_p = 7.50$. The values of the free energy functions used for titanium vapor were those computed by Gilles and Wheatley.[6] In the case of copper it was found that only the ground state of the atom made a significant contribution to the value of the electronic partition function.[7]
Experimental Errors.—For a single calculation of ΔH_0^0, the standard deviations of the measurable quantities were found to be

Temp., °C.	±1.5
Weight loss, g.	±0.0001
Eff. time, sec.	±60
Sample dimension, cm.	±0.0025

Using these values, calculation of the standard deviation for an individual value of ΔH_0^0 gives 74 cal. for titanium and 73 cal. for copper. These values are in good agreement with those calculated from the mean ΔH_0^0's of the experimental results.

(5) K. K. Kelley, "Contributions to Data on Theoretical Metallurgy: X, XI," Bulletins 476 (1949) and 477 (1950), U. S. Department of Interior, Bureau of Mines.

(6) P. W. Gilles and Q. de L. Wheatley, J. Chem. Phys., 19, No. 1, 129 (1951).

(7) C. R. Moore, "Term Designation for Excitation Potentials," Princeton University Observatory, Princeton, N. J., 1934.
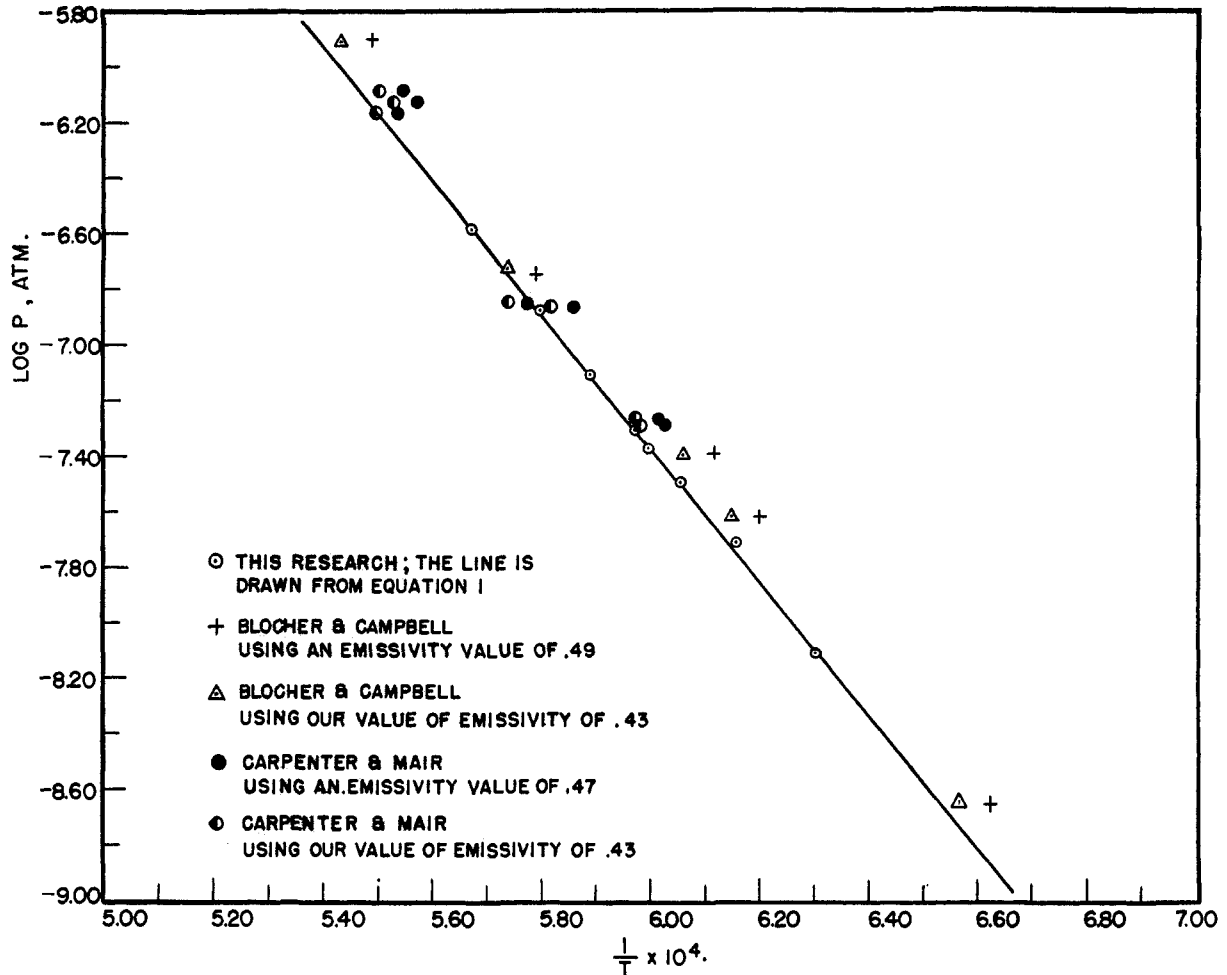
Fig. 1.—Vapor pressure of titanium.

This agreement suggests that there is no temperature trend in ΔH_0^0, and that the accommodation coefficient is unity within experimental error.

Experimental Results.—The data are given in Tables I, II, III and IV and plotted in Figs. 1 and 2. The curve for titanium (Fig. 1) was plotted by using the equation

$$\log P_{atm} = 7.7960 - 24644/T - 0.000227\ T \quad (1)$$

For copper (Fig. 2) it was drawn from the equation

$$\log P_{atm} = 6.9214 - 17546/T - 0.0001659\ T \quad (2)$$

The method of obtaining these equations is described in a previous paper.[2]

TABLE I

VAPOR PRESSURE OF TITANIUM

Run no.	Temp., °K.	Eff. time, sec.	Total wt. loss, g.	Eff. area, cm.²	Evap. rate, g. cm.⁻² sec.⁻¹ × 10⁸	Pressure, atm. × 10⁸
8	1587	24652	0.0233	15.8993	5.952	0.773
7	1624	6890	.01557	15.9284	14.187	1.864
1	1651	4493	.01749	15.9709	24.374	3.228
6	1667	4846	.02473	15.9800	31.935	4.251
2	1675	2983	.01803	15.9748	37.836	5.047
5	1698	3438	.03261	16.0987	58.919	7.914
3	1725	1895	.02988	16.1529	97.616	13.245
9	1764	2381	.07366	16.1206	191.907	26.269

TABLE II

HEAT OF SUBLIMATION OF TITANIUM

Run no.	Temp., °K.	$-R\ln P$, cal. deg.⁻¹ mole⁻¹	$-(F^0 - H_0^0/T)c$, cal. deg.⁻¹ mole⁻¹	$-(F^0 - H_0^0/T)g$, cal. deg.⁻¹ mole⁻¹	ΔH_0^0, cal. mole⁻¹
8	1587	37.1237	12.520	46.551	112925
7	1624	35.3745	12.688	46.678	112648
1	1651	34.2826	12.809	46.764	112660
6	1667	33.7357	12.877	46.815	112814
2	1675	33.3947	12.910	46.840	112769
5	1698	32.5005	13.007	46.910	112753
3	1725	31.4763	13.120	46.995	112721
9	1764	30.1161	13.280	47.111	112803

Mean $\Delta H_0^0 = 112763$ cal. mole⁻¹

Standard deviation = 83 cal.

TABLE III

VAPOR PRESSURE OF COPPER

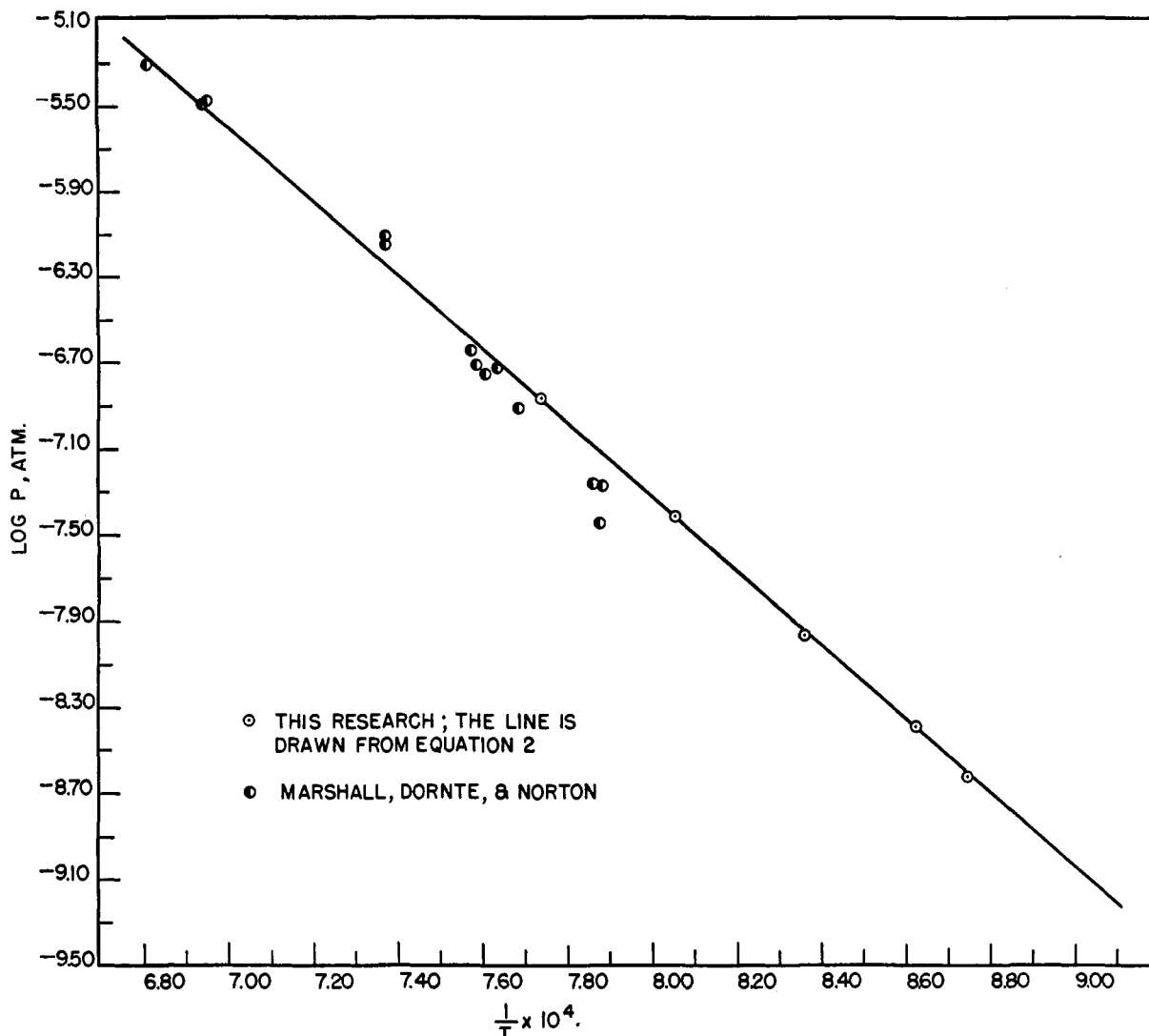| Run no.	Temp., °K.	Eff. time, sec.	Total wt. loss, g.	Eff. area, cm.²	Evap. rate, g. cm.⁻² sec.⁻¹ × 10⁸	Pressure, atm. × 10⁸
5	1143	23762	0.01949	33.6386	2.438	0.233
3	1159	23903	.03337	33.6825	4.145	0.399
2	1196	6566	.02387	33.7451	10.773	1.054
1	1241	1740	.02261	33.8070	38.437	3.831
4	1292	1947	.08872	33.8974	134.428	13.672

Fig. 2.—Vapor pressure of copper.

TABLE IV

HEAT OF SUBLIMATION OF COPPER

Run no.	Temp., °K.	$-R \ln P$, cal. deg.$^{-1}$ mole^{-1}	$-(F^0 - H_0^0/T)c$, cal. deg.$^{-1}$ mole^{-1}	$-(F^0 - H_0^0/T)g$, cal. deg.$^{-1}$ mole^{-1}	ΔH_0^0, cal. mole^{-1}
5	1143	39.4984	10.661	41.452	80341
3	1159	38.4299	10.744	41.520	80210
2	1196	36.5008	10.930	41.678	80430
1	1241	33.9366	11.147	41.860	80230
4	1292	31.4085	11.381	42.064	80222

Mean ΔH_0^0 = 80287 cal. mole^{-1}

Standard deviation = 86 cal.

The over-all accuracy of the data depends on the accuracy of the temperature scale of the standard lamp that is used.[8] With this consideration the standard deviation for an individual value of ΔH_0^0 is found to be 153 cal. for titanium and 152 cal. for copper.

Comparison with Earlier Data

The agreement between our data and the data

(8) The National Bureau of Standards set a maximum uncertainty of 5° at 800°, 3° at 1063°, and 7° at 2300° in the calibration of the lamp.

of Carpenter and Mair[9] and Blocher and Campbell[10] is fair, the disagreements being due, in part, to a difference in the emissivity values used in each case. To check this point, a determination of the emissivity of our titanium samples was made for each of the vapor-pressure runs, by comparing surface brightness temperatures with brightness tempera-

TABLE V

EMISSIVITY OF TITANIUM

Run no.	T, °K.	Average value of $e_{0.65\mu}$ for three readings per run, this research
8	1587	0.43
7	1624	.44
1	1651	.42
6	1667	.45
2	1675	.43
5	1698	.43
3	1725	.41
9	1764	.41

Av. value = 0.43

(9) L. G. Carpenter and W. N. Mair, Proc. Roy. Soc. (London). B64, 57 (1951).

(10) J. Blocher and I. Campbell, THIS JOURNAL, 71, 4040 (1949).

tures of the black body holes. The results are given in Table V.

Applying Carpenter and Mair's emissivity correction, we calculate an emissivity of 0.47. Blocher and Campbell[9] give a value of 0.49, while that given by Roeser and Wenzel[11] is 0.65. It is our opinion that the higher values obtained by Carpenter and Mair, Blocher and Campbell, and Roeser and Wenzel were influenced by oxide or nitride surface contamination.
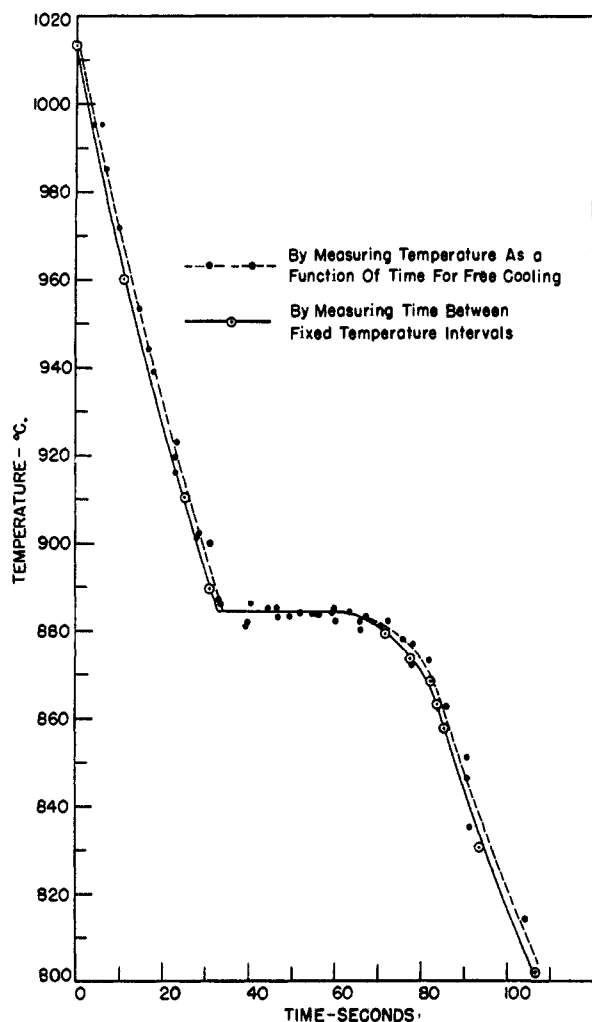

Fig. 3.—Cooling curve for titanium.

When Carpenter and Mair's data are treated with our emissivity coefficient of 0.43, their temperatures are increased by 13°. Similarly, Blocher and Campbell's temperatures are increased by amounts that vary from 14° at 1510°K. to 20° at 1822°K. When Carpenter and Mair's and Blocher and Campbell's vapor pressure data are replotted to these higher temperatures, their data come into closer agreement with ours, as shown in Fig. 1 (the temperatures assigned to our own data are not computed from emissivities). These new temperature assignments also change the values of ΔH_0^0, the average of the recalculated values of ΔH_0^0 being 112,167 cal./mole from Blocher and Campbell's data and 111,497 cal./mole from Carpenter and Mair's data.

The copper results are in general agreement with those of Marshall, Dornte and Norton.[12] Our value of ΔH_0^0 is somewhat lower than theirs which is ΔH_0^0 (mean) = 81086 ± 641 for the data plotted in Fig. 2, but at temperatures above 1356°K. (beyond the range of our own data) the results of Marshall, Dornte and Norton fall in line with extrapolation of our own vapor pressure equation (2), and so lead to values of ΔH_0^0 close to our own. It is felt that the general improvement in experimental technique accounts for the discrepancies in the lower temperature range.

Transition Point of Titanium

There was some uncertainty as to the character of the transition between α- and β-forms of titanium. Blocher and Campbell,[9] for example, were of the opinion that the transition was one of second order, and treated their data accordingly in evaluating ΔH_0^0. McQuillan,[13] on the other hand, reported the transition as first order at 882.5°. By means of cooling curves we have verified McQuillan's interpretation. Figure 3 shows our cooling curve data. The curves were taken by measuring the cooling rate of our titanium vapor pressure sample under high vacuum in the vapor pressure cell. Temperatures were determined with the optical pyrometer. The break occurs at 884 ± 3.5°, which is in quantitative agreement with McQuillan's measurement of 882.5°.

(11) "Handbook of Chemistry and Physics," 31st Ed., Chemical Rubber Publishing Co., 1949, pp. 2299, Table of Spectral Emissivities prepared by Roeser and Wenzel, National Bureau of Standards.

(12) A. L. Marshall, R. W. Dornte and F. J. Norton, THIS JOURNAL, 59, 1161 (1937).

(13) A. D. McQuillan, J. Inst. Metals, 78, 249 (1950).