imposing somewhat less stringent orientation requirements. It might also be predicted that the activation energy would be higher because of the greater strength of the S–O bond than the S–S bond. If it is assumed that the activation energy is proportional to the strength of the bond broken,[31] a very rough estimate might be made from the relation

$$E_{(\mathrm{SO_3^=} + \mathrm{SO_4^=})} = E_{(\mathrm{SO_3^=} + \mathrm{S_2O_3^=})}\left(\frac{\text{strength of S–O bond in } \mathrm{SO_4^=}}{\text{strength of S–S bond in } \mathrm{S_2O_3^=}}\right)$$

by estimating the bond strengths from thermochemical values for the heat of formation of $SO_4^=$ and $S_2O_3^=$ from gaseous atoms (assuming hydration effects cancel or are negligible). Taking the values 215.8, 145.5, 148.5, $-66.3$ and $-59.1$ kcal. mole$^{-1}$ as the heats of formation of sulfate, thiosulfate, sulfite, sulfur atoms and oxygen atoms, respectively,[32] the estimated bond strengths are S–O 126.4 and S–S 63.3 kcal./mole, and the estimated $E$ for the sulfate exchange is 28.7 kcal. mole$^{-1}$. If the frequency factor is the same for the sulfate exchange as for the thiosulfate exchange, this would result in a half-time for the reaction in 0.1 $M$ sulfite and 0.1 $M$ sulfate of 3400 years at 100°, of 20 days at 250° and of 1 hr. at 400°. Voge[3] has shown that no exchange occurs between sulfite and sulfate on heating in 0.1 $N$ acid or alkaline solution for 35 hours at 100° but has observed a slow exchange between sulfur dioxide and sulfur trioxide gases at 335°, which was catalyzed by water. Norris[33] has observed an exchange between sulfur dioxide and concentrated sulfuric acid with a readily measurable rate in the temperature range of about 200°, and with an apparent activation energy of 28.8 kcal. mole$^{-1}$. Huston and Norris[33] have found that the rate of exchange between intensively dried sulfur dioxide and sulfur trioxide gases is conveniently measurable in the range of 400 to 440° and, as indicated by Voge, that the reaction is heterogeneous and strongly catalyzed by water. It would be interesting to investigate the exchange of aqueous sulfite with sulfate in sealed tubes at temperatures above 250°.

**Acknowledgments.**—The authors wish to express their appreciation to Dr. E. L. King for helpful discussions during the course of these investigations.

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## Summary

The transfer of the outer sulfur atom of thiosulfate ion to sulfite ion occurs in the temperature range of 60–100° at a rate which is proportional to the first power of the sulfite concentration and also of the thiosulfate concentration. The rate and activation energy appear to be essentially independent of $p$H in the range from $p$H 5 to 14. The second order velocity constant is given by the relation $k = 2.3 \times 10^6 e^{-14,500/RT}$ liters mole$^{-1}$ sec.$^{-1}$.

The evidence indicates that the equilibrium of thiosulfate with sulfur and sulfite is not a part of the mechanism of sulfur transfer. Other factors to be considered with regard to the mechanism of this reaction are discussed.

A preliminary value of 15 kcal. mole$^{-1}$ for the activation energy of the exchange of sulfide ion with thiosulfate has been determined.

Previous evidence indicating that the sulfur atoms of thiosulfate are not chemically equivalent has been confirmed and extended to show that exchange between them does not occur in 5 hours at 125° nor when the thiosulfate is precipitated as triethylenediaminenickel thiosulfate and subsequently dissolved in hydrochloric acid.

A reproducible routine method of determining the relative specific activity of $S^{35}$ in barium sulfate precipitates is described.

MADISON 6, WIS. RECEIVED JUNE 26, 1950

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[31] J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

[32] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[33] Norris, THIS JOURNAL, **72**, 1220 (1950).

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

# Vapor Pressure of Inorganic Substances. IV. Tantalum between 2624 and 2943°K.[1]

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

Although there have been two previous investigations of the vapor pressure of tantalum,[2,3] the results were in considerable disagreement. We have, therefore, redetermined the vapor pressure of tantalum, in this Laboratory, using the method of I. Langmuir. The method and techniques used by us have been described in earlier papers[4] from this Laboratory.

**Procedure.**—A sample of better than 99.9% pure tantalum was obtained from the Fansteel Metallurgical Corp. An analysis, conducted by the manufacturer, showed that the principal impurities were carbon and iron and that neither of these was present to more than 0.03%.

The rate at which the surface of a sample of tantalum evaporated *in vacuo* was determined. The sample was in the form of a hollow cylinder one inch high by one inch diameter with a $^1/_8$ inch wall thickness. The ends of the cylinder were each covered with several split radiation shields made of tantalum sheet. This arrangement practically eliminated evaporation from the ends since the split shields did not heat efficiently. Three longitudinal holes drilled into the cylinder wall and one hole through the upper set of radiation shields served as black-body holes.

The sample was placed in an evacuated metal chamber and heated by radio frequency induction. Temperatures were measured by means of a carefully calibrated disappearing-filament optical pyrometer sighted on the four black-body

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[1] This work was supported in part by The Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] D. B. Langmuir and L. Malter, *Phys. Rev.*, **55**, 743 (1949).

[3] M. D. Fiske, *ibid.*, **61**, 513 (1942).

[4] (a) H. L. Johnston and A. L. Marshall, THIS JOURNAL, **62**, 1382 (1940); (b) R. B. Holden, R. Speiser and H. L. Johnston, *ibid.*, **70**, 3897 (1948); (c) R. Speiser and H. L. Johnston, Preprint No. 11, Thirty-First Annual Convention of the American Society for Metals, Cleveland, Ohio, Oct. 17–21, 1949.

holes. The maximum uncertainty of the temperature scale in the range of the investigation was about 8 degrees, based on a calibration by the National Bureau of Standards. The probable error of determinations, however, was 3°K. with an additional error of 2°K. introduced by the window correction. The surface temperature of the radiation shields was determined by correcting observed brightness temperatures for spectral emissivity.

The sample was weighed to within ±0.00014 gram before and after each run. During the investigation, the sample was found to increase in size from run to run, probably as a result of rapid heating and cooling. In calculating the effective surface area, it was assumed that thermal expansion was uniform so that the area at high temperature, $A_T$, was given by

$$A_T = A_r\left(1 + 2\frac{\Delta L}{L}\right) \qquad (1)$$

where the subscript $r$ refers to room temperature. The proportional linear thermal expansion, $\Delta L/L_0$, was determined earlier at this Laboratory[5] as

$$\Delta L/L_0 = 6.080 \times 10^{-6}\,(T - 291) + 7.50 \times 10^{-10}(T - 291)^2 \qquad (2)$$

where $T$ is the absolute temperature.

To account for small temperature fluctuations during each run and for evaporation during initial heating and final cooling, an averaging process was used to calculate the effective time, $t$, of each run.[4a] It was assumed that the rate of evaporation, $m(T)$, as a function of temperature, $T$, could be expressed by the equation

$$\log m(T) = a/T + c \qquad (3)$$

where $a$ and $c$ are constants obtained from the actual periods at high temperatures and from the weight losses of the various runs. Equation 3 was then used to calculate $m(T)$ and $m(T_{\text{av}})$ in the equation

$$t = \int m(T)\, \mathrm{d}t/m(T_{\text{av}}) \qquad (4)$$

where integration is performed graphically.

The effective total weight loss, $W_e$, was calculated from the total weight loss $W_t$ by the relation

$$W_e = W_t\left(\frac{\text{loss by cylinder}}{\text{loss by cylinder + loss by ends}}\right) \qquad (5)$$

wherein the parenthetical quantities were calculated from equation 3.

## Discussion of Results

The experimental results are summarized in Table I, and plotted in Fig. 1 as log $p$ vs. $1/T$, along with the data of Langmuir[2] and of Fiske.[3] The solid curve is computed from equation 9.

TABLE I

EVAPORATION OF TANTALUM

| Run | Temp., °K. | Effective time, sec. | Weight loss, g. Total | Weight loss, g. Effective | Effective area, sq. cm. | $m(T)$ g.-cm.$^{-2}$ sec.$^{-1}$ $\times 10^8$ | Pressure atm. $\times 10^9$ |
|---|---|---|---|---|---|---|---|
| 16 | 2624 | 15860 | 0.02484 | 0.0243 | 21.17 | 7.234 | 6.216 |
| 23 | 2638 | 17962 | .03359 | .0328 | 21.31 | 8.579 | 7.390 |
| 20 | 2760 | 3784 | .03724 | .0363 | 21.32 | 45.01 | 39.66 |
| 19 | 2839 | 2056 | .04892 | .0476 | 21.35 | 108.4 | 96.92 |
| 17 | 2888 | 3222 | .13329 | .1295 | 21.34 | 188.4 | 169.8 |
| 15 | 2925 | 2246 | .13074 | .1269 | 21.29 | 265.4 | 240.8 |
| 21 | 2948 | 2050 | .18158 | .1762 | 21.41 | 401.4 | 365.5 |

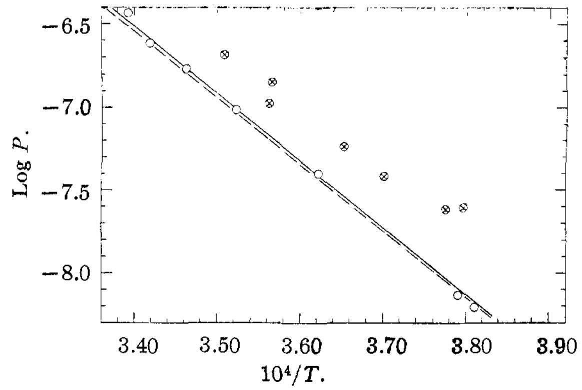

Fig. 1.—Vapor pressure of tantalum: — —, Langmuir and Malter; ⊗, Fiske; ○, this research; ——, this research, eqn. 9.

The reliability of the data was checked by computing values of $\Delta H_0^0$, the heat of sublimation at the absolute zero, from the several vapor pressure points by the equation

$$R \ln p = \left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}} - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{gas}} - \frac{\Delta H_0^0}{T} \qquad (6)$$

in which the parenthetical terms are the free energy functions for solid tantalum and for tantalum vapor, respectively. Values of the solid free energy function were obtained from the equation

$$(F^0 - H_0^0)/T = 559/T - 9.773 \times 10^{-4}\,T - 9.6591 \log T + 17.26 \qquad (7)$$

based on calorimetric data between 1100 and 2500°K.,[6] obtained in this Laboratory. Free energy functions for the vapor were computed statistically from the relationship

$$(F^0 - H_0^0)/T = R \ln[RT(2\pi mkT)^{3/2}/Nh^3] + R \ln Q_e \qquad (8)$$

where $Q_e$ is the electronic partition function[7] and the other symbols have their usual significance.[8] The results of these calculations are presented in Table II. The average value of $\Delta H_0^0$ thus obtained is 185.5 kcal., with a probable experimental error of 0.3 kcal. Values of $\Delta H_0^0$ were also calculated from

TABLE II

HEAT OF EVAPORATION OF TANTALUM

| Run no. | Temp., °K. | $-R \ln p$, cal. mole$^{-1}$ deg.$^{-1}$ | $-\left(\frac{F^0-H_0^0}{T}\right)_{\text{solid}}$, cal. mole$^{-1}$ deg.$^{-1}$ | $-\left(\frac{F^0-H_0^0}{T}\right)_{\text{gas}}$, cal. mole$^{-1}$ deg.$^{-1}$ | $\Delta H_0^0$, kcal. mole$^{-1}$ |
|---|---|---|---|---|---|
| 16 | 2624 | 37.55 | 18.12 | 51.379 | 185.8 |
| 23 | 2638 | 37.21 | 18.15 | 51.415 | 185.9 |
| 20 | 2760 | 33.87 | 18.47 | 51.722 | 185.2 |
| 19 | 2839 | 32.09 | 18.67 | 51.916 | 185.5 |
| 17 | 2888 | 30.98 | 18.80 | 52.034 | 185.5 |
| 15 | 2925 | 30.28 | 18.89 | 52.121 | 185.8 |
| 21 | 2948 | 29.45 | 18.94 | 52.175 | 184.8 |
| | | | | Av. | 185.5 |
| | | | | Deviation from mean | 0.3 |

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(5) James W. Edwards, Rudolph Speiser and Herrick L. Johnston, to be published soon in *J. Applied Phys.*

(6) G. W. Zeigler, Jr., R. Speiser and H. L. Johnston, to be published.

(7) Term designations and values taken from Charlotte E. Moore, "Term Designations for Excitation Potentials," The Princeton Observatory, Princeton, N. J., 1934.

(8) Values of physical constants used for all calculations are from R. P. 1634, National Bureau of Standards, February 1945.

TABLE III

HEAT OF EVAPORATION OF TANTALUM USING FISKE'S DATA FOR RATE OF EVAPORATION

| Temp., °K. | $m(T)$, g. cm.$^{-1}$ sec.$^{-1}$ $\times 10^8$ | $-R \ln p$, cal. mole$^{-1}$ deg.$^{-1}$ | $-\Delta\left(\frac{F^0 - H_0^0}{T}\right)$, cal. mole$^{-1}$ deg.$^{-1}$ | $\Delta H_0^0$, kcal. mole$^{-1}$ |
|---|---|---|---|---|
| 2633 | 28.8 | 34.80 | 33.26 | 179.2 |
| 2649 | 28.0 | 34.85 | 33.26 | 180.4 |
| 2700 | 43.8 | 33.94 | 33.26 | 181.4 |
| 2737 | 65.9 | 33.12 | 33.25 | 181.7 |
| 2804 | 160 | 31.33 | 33.25 | 181.1 |
| 2807 | 120 | 31.90 | 33.25 | 182.9 |
| 2850 | 230 | 30.59 | 33.24 | 181.9 |
| | | | Av. | 181.2 |
| | | | Mean deviation | 0.9 |

TABLE IV

HEAT OF EVAPORATION OF TANTALUM USING D. B. LANGMUIR AND L. MALTER'S DATA FOR RATE OF EVAPORATION

| Temp., °K. | $m(T)$, g. cm.$^{-1}$ sec.$^{-1}$ $\times 10^8$ | $-R \ln p$, cal. mole$^{-1}$ deg.$^{-1}$ | $-\Delta\left(\frac{F^0 - H_0^0}{T}\right)$, cal. mole$^{-1}$ deg.$^{-1}$ | $\Delta H_0^0$, kcal. mole$^{-1}$ |
|---|---|---|---|---|
| 2000 | 0.000163 | 59.08 | 33.28 | 184.7 |
| 2200 | .00978 | 50.85 | 33.28 | 185.1 |
| 2400 | .304 | 43.94 | 33.27 | 185.3 |
| 2600 | 5.54 | 38.09 | 33.27 | 185.5 |
| 2800 | 66.1 | 33.09 | 33.25 | 185.7 |
| 3000 | 579 | 28.71 | 33.22 | 185.8 |
| 3200 | 3820 | 24.90 | 33.19 | 185.9 |
| | | | Av. | 185.4 |
| | | | Mean deviation | 0.3 |

the rates of evaporation published by Langmuir and Malter[2] and by Fiske,[3] and these results are summarized in Tables III and IV. As is seen, the data of Langmuir and Malter are in exact accord with our own while Fiske's vapor pressures are somewhat high.

By use of equation 6, in conjunction with equations 7 and 8 and the average value of 185.5 kcal. for $\Delta H_0^0$, we obtain the vapor pressure equation

$$R \ln p = -(185.5 \times 10^3)/T + 3.7 \times 10^{-4}T - 8.4 \times 10^{-8}T^2 + 32.87 \quad (9)$$

where $p$ is pressure in atmospheres and $R$ is the gas constant in cal./mole/deg.

## Summary

The vapor pressure of tantalum was determined over the temperature 2624 to 2948°K. by measuring the rate at which a metal surface evaporates in vacuum. Values of $\Delta H_0^0$ were calculated from the individual vapor pressures and showed no appreciable trend, the average value being 185.5 ± 0.3 kcal. By combining this value with free energy functions for solid and gaseous tantalum, the following vapor pressure equation was obtained

$$R \ln p = -(185.5 \times 10^3)/T + 3.7 \times 10^{-4}T - 8.4 \times 10^{-8}T^2 + 32.87$$

Our experimental results agree accurately with the earlier work of Langmuir and Malter, but disagree with those of Fiske.

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

# The Vapor Pressure of Inorganic Substances. V. Zirconium between 1949 and 2054°K.[1]

BY GORDON B. SKINNER, JAMES W. EDWARDS AND HERRICK L. JOHNSTON

## Introduction

The vapor pressure of zirconium has been measured at this Laboratory by the vacuum evaporation method of Langmuir[2] as modified by Marshall, Dornte and Norton.[3] The method consists of measuring the rate at which a metal evaporates into a vacuum from a ring supported on a wire tripod and heated inductively by high frequency current.

Zirconium is difficult to volatilize apparently due to tightly adhering film that covers its surface even under relatively high vacuum conditions. We have overcome this obstacle by working at pressures of less than $2 \times 10^{-7}$ mm.

**Sample Purity.**—A sample of zirconium was vacuum cast from crystalline zirconium which was prepared by the iodide method and furnished through the courtesy of the Philips Research Laboratory of Eindehoven, Holland. A spectrographic analysis[4] showed that the final sample contained 0.99 atom per cent. of hafnium, 0.05 atom per cent. wolfram, and 0.37 atom per cent. of all other impurities including silicon and aluminum. Wolfram is known to have a lower vapor pressure than that measured for zirconium. Vapor pressures are not known for hafnium, but general chemical considerations indicate that its vapor pressures should be at most one-tenth those of zirconium at any given temperature. The presence of these two metals should make the measured vapor pressures of the zirconium sample approximately 1% low, but since this value lies within the experimental error of our data and since it would be partially compensated by the presence of low percentages of the more volatile impurities, such as aluminum, we have applied no correction.

## Experimental Apparatus and Procedure

The sample was machined to the form of an annular ring of about 1-in. o.d. by $^3/_8$-in. i.d. $^1/_2$-in. high, and was supported on three wolfram rods in the Pyrex apparatus shown in Fig. 1.

With the exception of the liquid air trap O, the system was baked out before each run. The charcoal trap was baked out for about 36 hours at 450° and the remainder flamed for 1 hour at about 400°. The apparatus was then

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

(2) I. Langmuir, *Phys. Rev.*, **2**, 329 (1913).

(3) Marshall, Dornte and Norton, THIS JOURNAL, **59**, 1161 (1937).

(4) Analyses were made by Mr. John Center, Chief Analyst of the Battelle Memorial Institute, Columbus, Ohio.