Discussion

The resonance energy for the tetrazole ring was calculated by combining our experimentally determined heats of combustion and heats of sublimation[30] with reported bond energy values[31] for four cases: tetrazole, 1,5-dimethyltetrazole, 1,5-diphenyltetrazole, 2,5-diphenyltetrazole. In these calculations, the C–N bond was assumed to be the standard type bond. Accurate information concerning bond energies in a molecule such as tetrazole is not available at this time. In considering the diphenyltetrazoles, the resonance energy of the phenyl groups was assumed to be additive and to have a value of 41 kcal. per phenyl ring. The resonance energies calculated for the four compounds were 55.6, 61.3, 65 and 70.3 kcal. per tetrazole ring, respectively. These values indicate that the resonance energy of the tetrazole ring is increased by the elimination of the tautomeric shift. This is an interesting point and should be investigated further. It will also be noted that the 2,5-disubstituted tetrazoles are more stable, 5 kcal. per mole, than the corresponding 1,5-disubstituted isomers (2 cases).

It would be of interest to have a larger number of 1,5- and 2,5-isomers to compare, and also to obtain additional sublimation data for the calculation of resonance energies. The comparison of the data in Table II again indicates the relative stability of compounds containing four nitrogen atoms in a ring compared to the isomeric non-cyclic structure.

TABLE II

	ΔH_c	ΔH_f
Nitroguanylazide	233.69	71.3
5-Nitroaminotetrazole	222.1 calcd.	59.7
Calcd. from guanidine salt	222.6	
Guanylazide nitrate	234.5	3.8
5-Aminotetrazole nitrate	224.1	−6.6
1,5-Diphenyltetrazole	1663.6	99.3
2,5-Diphenyltetrazole	1658.7	94.4
Formazane	1741.9	109.3

CHINA LAKE, CALIF.

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[30] Dr. F. M. Ernsberger and Mr. John Wiley of this Laboratory very kindly measured the vapor pressures of tetrazole, 1,5-diphenyltetrazole and 2,5-diphenyltetrazole for us by means of the Knudsen effusion technique. They found the following expressions to hold over the temperature range indicated:

for tetrazole

$$\log_{10}P = \frac{-5090}{T} + 15.79 \qquad (60\text{–}90^\circ)$$

for 1,5-diphenyl tetrazole

$$\log_{10}P = \frac{-6360}{T} + 17.20 \qquad (75-90^\circ)$$

for 2,5-diphenyltetrazole

$$\log_{10}P = \frac{-6250}{T} + 18.32 \qquad (60\text{–}80^\circ)$$

From these expressions ΔH's for sublimation were calculated to be:

tetrazole ΔH_S = 23.26 kcal./mole
1,5-diphenyltetrazole ΔH_S = 29.05 kcal./mole
2,5-diphenyltetrazole ΔH_S = 28.60 kcal./mole

[31] G. W. Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 75.

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

The Vapor Pressures of Inorganic Substances. VI. Vanadium Between 1666°K. and 1882°K.[1]

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

The vapor pressure of vanadium was determined over the temperature range 1666° to 1882°K. by measuring the rate at which a metal surface evaporates into a vacuum. Values of ΔH^0_0 were calculated from individual vapor pressures and showed no appreciable trend, the average value being 121.95 ± 0.14 kcal. By combining this value with a linear expression in T for the difference in free energy functions between solid and gaseous vanadium, the following vapor pressure equation was obtained: $R \ln p = \frac{-121.95 \times 10^3}{T} - 5.123 \times 10^{-4}\,T + 36.29$.

Introduction

The vapor pressure of vanadium has been determined in this Laboratory by the method first introduced by Langmuir[2] and later modified by Marshall, Dornte and Norton.[3] This method consists of measuring the rate at which a metal evaporates in a vacuum from a ring or cylinder heated to a constant temperature by radiofrequency induction.

Experimental Method

Apparatus and Procedure.—The techniques and apparatus we used are essentially similar to those described in earlier papers from this Laboratory.[4]

In the present investigation the Pyrex apparatus used was the same as that described in reference.[4e] The procedure was modified in two ways: (1) The apparatus was not sealed off from the diffusion and fore-pumps. (2) The optical pyrometer was calibrated after each run with the optical window in the line of sight, so as to determine the small temperature error introduced by condensation of metal on the window. This correction was negligible for the low temperature runs and reached a maximum value of 14° for the highest temperature runs. For a given run, the correction was assumed to be proportional to the time-at-high-temperature of the sample, since the shutter was opened for temperature readings at uniform time intervals.

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

[3] A. L. Marshall, R. W. Dornte and F. J. Norton, THIS JOURNAL, **59**, 1161 (1937).

[4] (a) H. L. Johnston and A. L. Marshall, *ibid.*, **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; (d) J. W. Edwards, H. L. Johnston and P. E. Blackburn, THIS JOURNAL, **73**, 172 (1951); (e) (V) G. B. Skinner, J. W. Edwards and H. L. Johnston, *ibid.*, **73**, 174 (1951).

Pressure in the system was in the range 2–4 × 10^{-7} before heating the sample. It rose into the 10^{-5} mm. range in each run as the sample was first heated and then fell off rapidly (in 3–5 min.) to the 10^{-6} mm. or 10^{-7} mm. range. We attributed most of this pressure rise to evolution of gases absorbed on various parts of the apparatus.[5]

Sample.—The sample was furnished through the courtesy of The United States Vanadium Corporation, Niagara Falls, N.Y., whose analysis showed V, 99.6%; C, 0.2%; H_2, 0.1%, and traces of Fe, Si, Mn, Cu, Ca, etc., making up the remaining 0.1%. It was in the form of a solid cylinder about 1.00 in. in diam. × 0.44 in. high, into which several black body holes had been drilled parallel to the axis, 30-mils. in diameter and about 0.3 in. deep.

Calculations.—Vapor pressures were calculated as described in reference 5.

Errors.—Standard (r.m.s.) deviations of the various measurements were determined as:

Temperature ± 1.8°
Effective area ± 1.5%
Effective time ± 0.6%
Weight loss ± 8 × 10^{-5} g.

As calculated by propagation of these observational errors, the standard deviation in ΔH_0^0 is 133 cal.; this is the consistency that can be expected of our data aside from errors in free energy functions. If we also take into account the maximum uncertainty in the temperature scale of the standard lamp we use (calibrated by the National Bureau of Standards) the standard deviation is increased to 186 cal. The standard deviation calculated from our experimental values of ΔH_0^0 is 138 cal.

Data

The experimental results and calculated pressures are summarized in Table I and plotted in Fig. 1 as log p *vs.* $1/T$. The curve was obtained from equation (1). In the treatment of the experimental data, pressures, p, were calculated according to the relation

$$p = \frac{\Delta W}{\alpha}\sqrt{\frac{2\pi RT}{M}} \qquad (1)$$

in which ΔW is the weight loss per cm.^{2} per sec., and α is the accommodation coefficient, which was assumed to have the value unity.

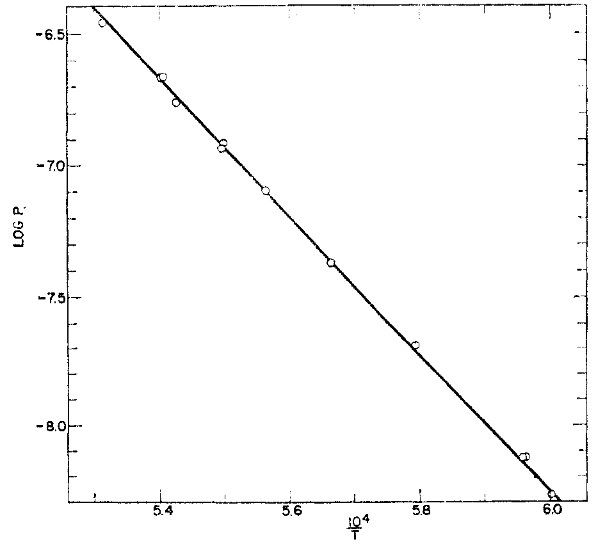

Fig. 1.—Vapor pressure of vanadium.

TABLE I

EVAPORATION OF VANADIUM

Run no.	Temp. in °K.	Effective time in sec.	Effective area in cm.^{2}	Weight loss in g.	Evap. rate, g. cm.$^{-2}$ sec.$^{-1}$ × 10^8	Pressure, atm. × 10^9
19	1666	19,964	16.62	0.01381	4.163	5.370
9	1677	21,161	17.00	.02079	5.779	7.479
8	1678	23,031	17.01	.02256	5.757	7.453
12	1726	19,069	16.78	.05003	15.64	20.53
20	1766	5,824	16.81	.03136	32.03	42.54
16	1798	5,015	16.81	.05031	59.67	79.97
13	1819	3,258	17.05	.05092	91.68	123.6
17	1820	2,088	16.99	.03076	86.73	116.9
11	1843	1,057	16.75	.02278	128.7	174.7
15	1850	1,589	16.83	.04283	160.1	217.7
14	1851	1,174	16.83	.03142	159.1	215.6
18	1882	1,531	16.63	.06453	253.4	347.5

The reliability of this assumption was checked by computing values of ΔH_0^0, the heat of sublimation, at absolute zero, from the several vapor pressures by the equation

$$R \ln p = \left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}} - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{gas}} - \frac{\Delta H_0^0}{T} \qquad (2)$$

in which the parenthetical terms are the free energy functions of solid and gaseous V, respectively. Values of the free energy function for the solid were obtained by combining Kelley's[6a] tabulated data and Anderson's[6b] low temperature heat capacity data for V. Free energy functions for the vapor were computed statistically from the relationship

$$\left(\frac{F^0 - H_0^0}{T}\right)_{\text{gas}} = R \ln \left[RT\frac{(2\pi mkT)^{3/2}}{Nh^3}\right] + R \ln Q_e \qquad (3)$$

TABLE II

HEAT OF EVAPORATION OF VANADIUM

Run no.	Temp. in °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.$^{-1}$	ΔH_0^0 kcal. mole^{-1}
19	1666	37.84	12.31	47.74	122.07
9	1677	37.18	12.36	47.78	121.75
8	1678	37.19	12.36	47.79	121.86
12	1726	35.18	12.55	47.97	121.86
20	1766	33.73	12.72	48.11	122.07
16	1798	32.47	12.84	48.22	121.99
13	1819	31.61	12.92	48.29	121.84
17	1820	31.72	12.93	48.29	122.09
11	1843	30.92	13.02	48.36	122.12
15	1850	30.48	13.04	48.39	121.79
14	1851	30.50	13.05	48.39	121.87
18	1882	29.55	13.16	48.49	122.10

Av. 121.95
Mean deviation ±0.123 cal
Standard deviation ±0.138 cal.

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[5] The pressure due to residual gas in the system was measured wih a D.P.I. Ionization Gauge HG 200 with VG 1A tube. In several initial runs, gas was evolved continuously from the sample during heating, and the calculated vapor pressures were in some instances as much as 10% too high. For this reason, these initial runs were not considered in final evaluation of the data.

[6] (a) K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy," Bur. of Mines, Bull. No. 476 (1949) and Bull. No. 477 (1950); (b) C. T. Anderson, THIS JOURNAL, **58**, 564 (1936).

in which Q_e is the electronic partition function,[7] m is the mass of the atom in grams, and the other symbols have their usual significance.[8]

The results of these calculations are presented in Table II, the average value of ΔH_0^0 being 121.95 kcal. per mole, with a standard deviation from the mean of 0.14 kcal. The absence of a trend in the calculated values of ΔH_0^0 indicates that α is unity.

Using equation (2), in conjunction with a linear equation in T for the difference in the free energy functions, and an average value of 121.95 kcal. for ΔH_0^0, we obtain the vapor pressure equation

$$R \ln p = \frac{-121.95 \times 10^3}{T} - 5.123 \times 10^{-4}T + 36.29 \quad (4)$$

where p is the pressure in atmospheres and R is the gas constant in cal. mole^{-1} deg.$^{-1}$.

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[7] Term designations and values were taken from Charlotte E. Moore, "Term Designations for Excitation Potentials," Princeton Observatory, Princeton, N. J., 1934.

[8] Values of physical constants used were taken from Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research, Natl. Bur. Standards*, **34**, 143 (1945); also designated as Research Paper RP 1634.

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

The Vapor Pressures of Inorganic Substances. VII. Iron Between 1356°K. and 1519°K. and Cobalt Between 1363°K. and 1522°K.[1]

BY JAMES W. EDWARDS, HERRICK L. JOHNSTON AND WALTER E. DITMARS

The vapor pressures of iron and cobalt have been determined by the vacuum evaporation method introduced by Langmuir. Heats of sublimation at the absolute zero have been calculated and equations formulated for vapor pressure as a function of temperature. The condensation (accommodation) coefficient has been found to be unity.

Introduction

The vapor pressures of iron and cobalt have been determined in this Laboratory by the method of vacuum evaporation[2] from cylinders heated inductively. Our data constitute the first measurements reported for cobalt, but measurements on iron were carried out previously by Jones, Langmuir and Mackay,[3a] and by Marshall, Dornte and Norton.[3b]

Experimental Method

Apparatus and Procedure.—Techniques and apparatus used were essentially similar to those described in earlier papers from this Laboratory[4] although a new Pyrex apparatus was built for these runs with some modification from the previous design. The most marked modification was use of a suspension wire (0.020 inch tantalum) to support the iron and cobalt cylinders from above. The disk shaped iron sample was supported from below on the tips of three wolfram rods.

The Pyrex cell was baked out at about 400° with the sample in place for at least two hours before each run, by placing a removable oven around it. During a preliminary evacuation, prior to the bakeout, a charcoal trap in communication with the cell was heated to about 300° under vacuum to drive off most of the gases, and then the entire system was flushed three times with C.P. hydrogen. As a check of experimental results, C.P. hydrogen to a pressure of 20 mm. was also admitted during the bakeout of the Pyrex cell in one run (No. 9). With this preliminary heat treatment we were able to maintain pressures in the neighborhood of 5×10^{-7} mm. during evaporation runs, with liquid air around the charcoal trap.

The apparatus was opened after each run by cutting the upper portion of the Pyrex cell with a hot wire glass cutter. When it was then closed by fusion, some components of the Pyrex glass were volatilized and condensed on the optical window forming a barely visible white coating. Experiment showed that in one instance this coating required a temperature correction of 3.5°. The correction could not be expected to be constant, however, and so it was determined for each run individually by calibrating the optical pyrometer used for temperature measurement against a standard lamp with the window in the line of sighting. The correction was essentially independent of the time and temperature of the run.

Independent checks of the pyrometer calibration were obtained by: (1) observing the temperature of a black body immersed in freezing copper (an N. B. S. standard freezing point sample); and (2) intercomparing the standard lamp and another optical pyrometer that had been calibrated at the National Bureau of Standards. The three temperature scales were in agreement within the experimental error.

Samples.—The iron was an especially pure sample prepared for us by the Philips Research Laboratory of Eindhoven, Holland. The cobalt was produced by the Kulite Tungsten Company, New Jersey.

One iron sample was in the form of a solid cylinder of 1.3400-in. height and 0.8110-in. diam.; the other was a solid disk of 0.5354-in. height and 1.0010-in. diam. A black body hole was drilled into each sample near the edge; in the cylinder it had a 0.05-in. diam. and 0.70-in. depth and in the disk a 0.040-in. diam. and 0.30-in. depth.

Spectroscopic analysis[5] of the vacuum cast iron gave the following percentages:

Co — Not detected
Mo — Not detected
Si — From 0.001 to 0.01
Ni — < 0.001
Cu — From 0.001 to 0.01
Al — From 0.001 to 0.01
Mn — Not detected
Ca — < 0.001
Fe (by difference) — 99.97.

The cobalt sample was in the form of a solid cylinder of 1.1048-in. height and 0.6970-in. diam. A 0.050-in. black body hole was drilled near the edge, to a depth of about 0.51 in. We found that putting a few very small metal turnings from the sample material into the hole broke up reflectivity from the bottom and produced a nearly perfect black body condition. Spectroscopic analysis[5] of the cobalt showed the percentages

Fe — From 0.01 to 0.1
Mo — Not detected
Si — From 0.005 to 0.05
Ni — From 0.05 to 0.5
Cu — From 0.005 to 0.05
Al — From 0.001 to 0.01
Mn — From 0.005 to 0.05
Ca — < 0.001
Co (by difference) — 99.25.

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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] *Cf.* references (1) and (2) of paper No. VI in this series.

[3] (a) H. A. Jones, I. Langmuir and G. M. J. Mackay, *Phys. Rev.*, **30**, 201 (1927); (b) A. L. Marshall, R. W. Dornte and F. J. Norton, THIS JOURNAL, **59**, 1161 (1937).

[4] *Cf.* reference 3 of paper No. VI of this series.

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