JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 70A, No. 2, March–April 1966

Vapor Pressure and Heat of Sublimation of Rhenium[1]

E. R. Plante and R. Szwarc[2]

Institute for Materials Research, National Bureau of Standards, Washington, D.C.

(October 27, 1965)

The vapor pressure of rhenium was measured by the Langmuir method in the temperature range 2350–3050 °K using a vacuum microbalance. The least squares line through the four series of data points is $4.5756 \log P(\text{atm}) = 32.26 - 180700/T$. Least squares lines for each of the four series yield heats and entropies of sublimation higher than the corresponding third law values. The vapor pressure equation based on the average heat and entropy is, $4.5756 \log P(\text{atm}) = 33.36 - 183500/T$.

The selected third law heat of sublimation, ΔH_S° (298) is 185.9 kcal mol^{-1}. Our recommended equation for the vapor pressure is $4.5756 \log P(\text{atm}) = 31.86 - 180200/T$ based on our mean third law heat and tabulated values for the entropies and enthalpies.

Key Words: Heat of sublimation, Langmuir vaporization, rate of vaporization, rhenium, vapor pressure.

1. Introduction

The only published experimental data on the rate of sublimation of rhenium is due to Sherwood et al., [1].[3] Their data were obtained by the Langmuir method using a modification of the hot wire technique and utilizing an emissivity correction to obtain absolute temperatures.[4] Although there is no special reason to question the accuracy of their results, past experience has shown that large systematic errors often occur and are difficult to detect in high temperature vaporization measurements. Hence, in view of this and the interest in rhenium as a useful material for particular high temperature applications, it was considered worthwhile to undertake additional measurements.

2. Experimental Method

The specimen used in this work came from a sample of zone refined rod supplied by MRC Corporation, Orangeburg, New York and was fabricated by arc erosion at NBS into a right circular cylinder about 1.5 cm long and 0.25 cm in diameter. A hole 0.1 cm in diameter and 1.0 cm long, assumed to represent blackbody conditions, was drilled along the cylinder axis and a suspension hole 0.025 cm in diameter was drilled along a diameter near the other end of the sample.

A "typical" analysis according to the supplier showed the principal metallic impurities to be Fe, Mo, and Si with impurity contents of <10, 40, and 10 PPM, respectively, while the principal nonmetallic impurity was 12 PPM O_2.

A semiquantitative spectrochemical analysis performed at NBS indicated the presence of Cu and Si in the range of 10–100 PPM and Ca, Fe, and Mg in the range of 1–10 PPM.

The density of a piece of the rhenium stock was determined by weighing in water and was 20.95 g cm^{-3}, close to the theoretical x-ray density of 21.04 g cm^{-3} [2].

The measurements were made using the vacuum microbalance apparatus previously described [3]. Samples were heated directly by rf induction at 450 kHz. Vacuum in the ultra-high vacuum range (10^{-7} to 10^{-9} torr) was maintained by a 90 liter per second ion pump. Weight losses in the microgram range were determined by measuring balance beam displacement with a cathetometer.

The sample was suspended from one arm of an equal-arm quartz beam microbalance at the end of a chain of 0.025 cm diam fused silica and sapphire rods by a loop of 0.0075 cm diam tungsten wire which passed through the suspension hole in the sample and over a hook on the lowest rod. The chain of sapphire and fused silica rods was connected at each end by V-shaped hooks made by heating and bending the rods.

The arm of the vacuum chamber in which the sample hung was a 16 mm O.D. fused silica tube with a graded seal and Pyrex window at the bottom for temperature measurement. The window was protected from vapor deposition during the sublimation experiments by a magnetically operated shutter.

---

[1] This work was supported in part by the National Aeronautics and Space Administration.

[2] Present Address: Department of Materials Science, University of Cincinnati, Cincinnati, Ohio.

[3] Figures in brackets indicate the literature references at the end of this paper.

[4] All temperatures in this paper are based on the 1948 IPTS.

A Vycor sleeve of 13 mm O.D. fitted snugly inside the 16 mm O.D. fused silica tube of the vacuum system. A thin platinum coating deposited on the inner surface of this sleeve helped prevent static charge buildup in the vicinity of the sample from interfering with the weighing but did not heat inductively.

An NBS-calibrated optical pyrometer with a magnifying objective lens was used to measure temperatures by sighting on the blackbody hole through the calibrated window and mirror. Calibration corrections for the mirror and window were determined in situ, before and after a series of experiments, by sighting the pyrometer on a band lamp located above the vacuum apparatus on a rotatable mount. With the pyrometer and band lamp in one position, readings on the band lamp filament could be made using the same optical path as was used during the vapor pressure measurements except that the source was further away. By rotating the band lamp 90 degrees and raising the pyrometer, temperature readings could be made directly on the band lamp filament. The calibration correction was obtained from the difference between reciprocal absolute temperatures with and without the window and mirror in the optical path.

In obtaining each datum point the following sequence of operations was performed: (1) The rest point of the microbalance was determined, (2) the sample was slowly heated to a temperature several hundred degrees below the temperature of the experiment, (3) the sample was rapidly heated to the operating temperature and maintained as nearly constant as possible, (4) the sample was rapidly cooled to a temperature well below the experimental temperature, the power slowly reduced, and the oscillator then turned off, and (5) the rest point of the balance was redetermined. The slow heating and cooling portions of the cycle were necessary to avoid lateral motion of the specimen caused by the rf field while the rapid heating and cooling portions of the cycle made the measurement of the duration of the experiment more accurate. The duration of the experiment was measured from the time the oscillator was set at a predetermined power setting to the time the power was decreased. Hence, the deficiency in vaporized material resulting from the fact that the sample is not yet at temperature at zero time is compensated for by the excess of material vaporized after the experiment has been terminated. The mass change of the sample was determined from the displacement of the beam of the microbalance and the previously determined sensitivity of the balance which was about 0.5 micrograms/micron.

The change in sensitivity with load was sufficiently small so that the weight change of the sample during a series of experiments had negligible effect. As in our previous studies [4, 5] duplicate rest points usually agreed to within $\pm 2\ \mu$: however, on several occasions during the present experiments, long term drifts of 20 to 30 μ were noted, indicating that errors due to the weight loss measurement could become important for the experiments with the smaller weight losses.

3. Data and Thermodynamic Treatment

Vapor pressures were calculated using the equation:[5]

$$P=\frac{m}{\alpha\ at}\left(\frac{2\pi RT}{M}\right)^{1/2} \tag{1}$$

where m is the mass of material sublimed, t is the duration of the experiment, a is the projected surface area of the sample, T is the absolute temperature, R is the gas constant, M is the atomic weight of the vaporizing species, monatomic rhenium, and α is the vaporization coefficient, which was assumed equal to unity. The value of the sample area a, at temperature T was calculated from the area measured at room temperature a_0, by assuming that the equation $a=a_0[1+2\beta(T-300)]$ was valid in the temperature range where vapor pressure measurements were carried out. In this equation β is the coefficient of linear thermal expansion which was assumed to be 7.2×10^{-6} $^\circ\mathrm{K}^{-1}$ based on the work of Sims et al., [2]. The sample area at room temperature a_0, is calculated from the measured length and diameter of the cylindrical specimen.

In general, the heat of sublimation can be computed from vapor pressure data in two ways. In the second law method, one can make use of the experimental data to evaluate both constants in the equation

$$\log P(\mathrm{atm})=-\frac{\Delta H^\circ}{R'T}+\frac{\Delta S^\circ}{R'} \tag{2}$$

where ΔH° is the heat of sublimation at the average temperature, ΔS° is the entropy change at the same temperature and R' is equal to $R\ln 10$. It should be noted that this equation is only approximate since it ignores the temperature dependence of ΔH° and ΔS°. Although a more exact second law treatment can be made by inclusion of the temperature dependence of ΔH° and ΔS°, the error introduced into the second law heat and entropy of sublimation by use of eq (2) in the present case is small in comparison with the error in these quantities resulting from scatter in the vapor pressure data. As a matter of interest, a correct second law treatment for each series of data in the present work was carried out and the values for ΔH° and ΔS° at the average temperatures agreed within 0.1 kcal mol^{-1} and 0.05 cal mol^{-1} $^\circ\mathrm{K}^{-1}$ with those obtained from the simpler treatment.

In the third law method, one makes use of absolute entropies, usually obtained from heat content and spectroscopic data, to calculate the entropy change for the assumed sublimation process at each temperature. These values and the experimental pressures can then be substituted in eq (2) to obtain the experimental values of ΔH° at the specified temperatures. In practice, use is generally made of free energy functions which allow one to calculate a value for the

---

[5] Values of constants used in the calculations were: $R=1.98717$ cal mol^{-1} $^\circ\mathrm{K}^{-1}$, or 8.3143 J $^\circ\mathrm{K}^{-1}$ mol^{-1}: atomic weight of rhenium 186.2: one standard atmosphere $=101.325$ N/m^2.

heat of sublimation at a reference temperature, usually 298.15 °K (or 0 °K) according to the equation,

$$\Delta H_s^\circ = T\left[\left(\frac{G_T^\circ - H_{298}^\circ}{T}\right)_c - \left(\frac{G_T^\circ - H_{298}^\circ}{T}\right)_g - R\ln P(\text{atm})\right] \quad (3)$$

where $\left(\frac{G_T^\circ - H_{298}^\circ}{T}\right)$ is the free energy function. Differences between $\Delta H_s^\circ(298)$ obtained by the second law and the third law methods can give information concerning the consistency of the vapor pressure data obtained, the free energy function data used, the sublimation reaction assumed, or the existence of a vaporization coefficient other than unity. Frequently, a lack of trend in the heat of sublimation calculated as a function of the experimental temperature is taken as an indication that no important systematic errors are present in the data. Actually, because of random error in the data points and limited temperature ranges, it is usually easier to find a discrepancy by comparing second and third law heats of sublimation or the experimental entropy change with that found from heat content and spectroscopic data.

4. Results

The basic data from four series of sublimation experiments are listed in table 1. The major differences between the first two series and the last two series of measurements are that different pyrometers were used for temperature measurements and different observers made the temperature and weight loss measurements. In addition to these differences, determinations of the window and prism factors ("*A*" values) before and after each of the first three series of measurements indicated that substantial increases in these quantities had taken place. It did not prove possible to determine what was responsible for the increase in *A* values. It is believed that a sufficient temperature gradient exists in the sample region of the vacuum system during measurements so that any Re_2O_7 in the sample region would evaporate and be able to migrate past the shutter to the sight window. An Re_2O_7 contaminant could have been introduced into the sample region of the vacuum system from the sample itself, by oxidation of Re metal during glassblowing when the window was replaced after the series I measurements, or by oxidation of Re metal by H_2O_2 which was used after the series I and II measurements to remove small amounts of rhenium not collected by the Vycor insert tube. Another possibility is that Re reacted with the Vycor insert tube to form $ReO_2(g)$ and a stable rhenium silicide. Calculation indicates that rhenium disilicide is sufficiently stable so that $ReO_2(g)$ might be formed in appreciable quantities assuming its standard free energy of formation is zero, if the temperature of the rhenium-Vycor interface were 1400 °K or higher. An x-ray diffractogram of material scraped from the side of the Vycor insert tube at the conclusion of the series III data indicated the presence of a phase other than Re which, however, could not be identified as either $ReSi_2$, ReSi, SiO_2, or a Pt-Re alloy.

TABLE 1. *Vapor pressures and heats of sublimation of Rhenium* [a]

Temp.	Duration of run	Wt. loss [b]	Vapor pressure	$\Delta H_s^\circ(298)$
		Series I		
°K	*sec*	*μg*	*atm × 10⁹*	*Kcal mol⁻¹*
3058	240	5563	1280	185.5
2624	900	166	9.46	185.6
2707	540	248	23.9	186.3
2794	300	398	70.1	186.2
2837	245	584	127	185.6
		Series II		
2541	1800	141	3.97	184.3
2491	2400	92.5	1.94	184.3
2627	600	156	13.4	184.0
2712	300	241	42.0	183.6
2812	240	638	141	183.4
2686	300	181	31.4	183.5
2633	600	179	15.4	183.7
2405	240	26.7	0.550	184.2
2348	10800	51.8	.235	183.9
		Series III		
2435	5400	56.8	0.524	186.6
2559	1800	140	3.96	185.6
2645	1200	292	12.6	185.6
2550	1800	121	3.42	185.7
2674	720	252	18.2	185.6
2942	300	2663	482	184.4
2782	360	483	71.0	185.3
2492	3600	108	1.51	185.7
2462	4800	100	1.04	185.3
2351	10800	40.1	0.182	185.3
2401	5400	36.8	.337	186.3
2857	270	906	180	184.8
		Series IV		
2620	1200	189	8.13	186.1
2636	1200	238	10.3	186.0
2664	1200	362	15.7	185.7
2661	1200	320	13.9	186.1
2646	1200	270	11.7	186.0
2650	1200	268	11.6	186.3
2659	1200	285	12.3	186.6
2543	2400	128	2.71	186.4
2585	1200	132	5.64	185.6
2647	1200	260	11.2	186.3
2509	3600	113	1.59	186.7
2687	720	284	20.6	185.8
2442	7200	102	0.707	185.7
2729	420	332	41.6	184.8
2580	1500	177	6.04	184.9

[a] Listed in experimental sequence.

[b] Room temperature sample surface areas were 1.597, 1.591, 1.590, and 1.587 cm^2 for series I through IV, respectively.

Evidence that the observed increase in *A* value was not simply due to deposition of Re on the window was obtained from the series IV data in which about 3450 μg of Re was vaporized with no measurable change in the *A* value of the window and during a series of experiments performed between series III and IV during which 2000 μg of Re were vaporized without the shutter interposed between the sample and the window with no resulting change in *A* value. Likewise, the fact that the increase in *A* values for the series I, II, and III data was all about the same while the total amount of Re vaporized was about 7000, 1150, and 6000 μg, respectively, is inconsistent with this hypothesis. Initially, it was thought that the change in A value had taken place during preliminary outgassing by volatilization of a rhenium oxide contaminant and that the A value measured at the end of the series was the appropriate one to use. However, analysis of the least squares residuals for the series II and series III data show a trend suggesting that at least part of the shift took place during the series. Therefore, for each of the first three series of measurements, the average of the A values determined before and after the series was used to correct the observed temperature to absolute temperature.

It should be noted that the adoption of any constant A value will have practically no effect on the heat of sublimation calculated by the second law method while the third law heat will be changed if the A value is changed as will the second law entropy. Also, if the temperatures are varied randomly during the series, a systematically changing A value will have little effect on the second law heat.

Table 2 summarizes the second law heats and entropies of sublimation calculated by least squares for each series of data in the present work and adjusted to temperatures of 298 and 2600 °K, respectively, using Stull and Sinke's tables [6]; similarly adjusted values based on those reported by Sherwood et al. [1]; mean third law heats of sublimation based on the free energy functions listed by Stull and Sinke; and the standard errors computed for each of these quantities as well as the estimated overall uncertainty in the third law heats of sublimation.

The final heat and entropy of sublimation based on the second law method were obtained by averaging the individual results obtained in the four series of experiments. These values lead to the equation $4.5756 \log P(\mathrm{atm}) = 33.36 - 183500/T$ which can be used to represent the vapor pressure of rhenium in the temperature range (2350–3050 °K).

TABLE 2. *Heat and entropies of sublimation of rhenium*

Determination	Second law values				Third law values		
	$\Delta H_s^\circ(298)$ kcal mol^{-1} (kJmol^{-1})	Standard error kcal mol^{-1} (kJmol^{-1})	$\Delta S_s^\circ(2600)$ [a] cal mol^{-1} °K^{-1} (Jmol^{-1} °K^{-1})	Standard error cal mol^{-1} °K^{-1} (Jmol^{-1} °K^{-1})	$\Delta H_s^\circ(298)$ kcal mol^{-1} (kJmol^{-1})	Standard error kcal mol^{-1} (kJmol^{-1})	Overall uncertainty kcal mol^{-1} (kJmol^{-1})
Series I	188.4 (788.1)	3.4 (14.2)	32.76 (137.1)	1.22 (5.1)	185.8 (777.5)	0.2 (0.7)	1.7 (6.9)
Series II	188.2 (787.5)	1.6 (6.6)	33.53 (140.3)	0.61 (2.5)	183.9 (769.4)	0.1 (0.5)	1.4 (5.9)
Series III	190.9 (798.9)	1.9 (7.9)	33.94 (142.0)	0.73 (3.1)	185.5 (776.2)	0.2 (0.7)	1.3 (5.4)
Series IV	189.4 (792.6)	5.1 (21.4)	33.20 (138.9)	1.96 (8.2)	185.9 (778.0)	0.1 (0.6)	0.6 (2.7)
Sherwood et al., [1]	193.0 (807.6)	[b] 6.0 [b] (24.9)	34.56 (144.6)	[b] 2.21 [b] (9.2)	185.7 (776.8)	[b] 0.4 [b] (1.6)	[c] 1.2 [c] (4.8)
All points this work	186.6 (780.6)	2.6 (11.0)	32.32 (135.2)	1.00 (4.2)	185.3 (775.5)	0.2 (0.6)	[c] 0.5 [c] (1.9)
Final	189.2 (791.7)	[c] 1.9 [c] (7.8)	33.36 (139.6)	[c] 0.64 [c] (2.7)	185.9 (778.0)	0.1 (0.6)	0.6 (2.7)

[a] Calculated from Stull and Sinke [6]. $\Delta S_{2600}^\circ = 31.86$ cal mol^{-1} °K^{-1}.
[b] These standard errors were calculated from the data given in [1].
[c] These error estimates are 3 × standard error.

The final heat of sublimation is the mean third law value obtained from the series IV data. This heat and the tabulated entropy at 2600 °K lead to the equation $4.5756 \log P(\mathrm{atm}) = 31.86 - 180200/T$. These two equations yield the same pressure at 2267 °K and gradually divergent pressures as the temperature increases or decreases. At 3000 °K the equation based on the second law values predicts a pressure of Re(g) about 20 percent higher than the equation based on the third law values.

All of the second law heats of sublimation tabulated in table 2 are higher than the mean third law heats reflecting the fact that the second law entropy changes are greater than the value based on the tables. Among the possibilities which could account for this fact is that the vapor above Re(c) contains vapor species other than Re(g), the tabulated entropy and free energy functions for Re(c) are too high, or a systematic error occurred in temperature measurements due to nonblackbody conditions in the "blackbody hole" of the sample. However, the difference between the second law entropies and third law entropy are not very large and it is questionable as to whether or not the differences are significant. For example, two or three standard errors are frequently accepted as a reasonable measure of the uncertainty in a value and within these limits, agreement of the second and third law heats and entropies of sublimation is satisfactory. The least squares line through all four series of data is $4.5756 \log P(\mathrm{atm}) = 32.26 - 180700/T$, which yields values of the heat and entropy of sublimation in excellent agreement with the tabulated entropy and the third law heat based on the tabulated entropy. The only reason for not recommending these values is that serious biases can be introduced into second law treatments when sets of data points having slight systematic differences are treated as a single set. This is particularly true when the data involved cover different temperature ranges. Since we would not recommend the second law heat and entropy derived in this way if it led to poorer agreement between the second and third law values, it would be rather arbitrary to recommend them because they are in better agreement.

The standard errors (standard deviations in the mean) listed in table 2 are computed from the scatter of the individual determinations about the mean or fitted line. The overall uncertainties for the third law heats of sublimation are the square root of the sum of the squares of the uncertainties arising from random scatter in the data points, uncertainty due to pyrometer calibration and uncertainty in the A value.

The uncertainties due to random scatter are taken as three times the standard error while that in the pyrometer calibration is based on the overall uncertainty listed on the NBS calibration certificate. For the first three series of data the overall uncertainty in the A values were assumed to be equal to one-half of the increase in the A value that took place during each series. For the series IV data the uncertainty in the A value was three times the standard error.

The uncertainties due to pyrometer calibration and A value were converted to equivalent uncertainties in the third law heat using the mean value of ΔH_s° (298) and the mean temperature for the series. These were then combined with the random uncertainty to yield the overall uncertainty listed in the last column of table 2.

In terms of uncertainties in temperature, the uncertainties in the pyrometer calibration, A value, random scatter and the overall temperature uncertainty were: series I−7, 22, 9, 25 °K; series II−6, 19, 4, 20 °K; series III−6, 16, 6, 18 °K; and series IV−6, 2, 6, 9 °K.

5. Summary and Conclusions

The mean third law heat of sublimation selected from the data in the present study as the most reliable is in excellent agreement with the mean value derived from the data of Sherwood et al. [1], while the agreement between the second and third law heats of sublimation is somewhat improved.

The question as to whether the second or third law heat of sublimation is the more reliable in the present case appears to be worthy of comment.

For metallic rhenium, heat content data obtained by conventional methods is available only to 1474 °K. Low temperature calorimetric data reported by Smith, Oliver, and Cobble [7] agrees within about one-half percent with the high-temperature data of Jaeger and Rosenbohm [8] in the range 0–20 °C. High temperature heat capacity data obtained by Taylor and Finch [9] in the range 300 to 2200 °K by the pulse heating method is systematically lower than the data of Jaeger and Rosenbohm; however, the estimated uncertainty of the former data is ±4 percent while that of the latter is ±0.5 percent and the data are in satisfactory agreement within these error limits. Between 1500 and 2600 °K, the contribution of the extrapolated heat capacity data to the free energy function and entropy of Re(c) is 3.34 and 4.53 cal mol^{-1} °K^{-1}, respectively, or about 20 percent. Hence, an extremely pessimistic view of the errors involved in the heat capacity of Re(c) would be necessary in order to justify the preference of the second law results. Because of this, the vapor pressure equation based on the third law heat of sublimation and tabulated entropies is recommended.

6. References

[1] E. M. Sherwood, D. M. Rosenbaum, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. **102,** 650 (1955).

[2] C. T. Sims, C. M. Craighead, and R. I. Jaffee, J. Metals (AIME Trans. 203) **7,** 168 (1955).

[3] N. J. Carrera, R. F. Walker, W. Nalley, and C. Steggerda, Vacuum Microbalance Techniques, Vol. **3,** p. 153, K. Behrndt, ed., (Plenum Press, New York, N.Y., 1963).

[4] N. J. Carrera, R. F. Walker, and E. R. Plante, J. Res. NBS **68A** (Phys. and Chem.) No. 3, 325 (1964).

[5] R. Szwarc, E. R. Plante, and J. J. Diamond, J. Res. NBS **69A** (Phys. and Chem.) No. 5, 407 (1965).

[6] D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, American Chemical Society, Washington, D.C. (1956).

[7] W. T. Smith, Jr., G. D. Oliver, and J. W. Cobble, J. Am. Chem. Soc. **75,** 5785 (1953).

[8] F. M. Jaeger and E. Rosenbohm, Koninkl. Akad. Wetenschap. Amsterdam, Proc. Sect. Sci. **36,** 786 (1933).

[9] R. E. Taylor and R. A. Finch, J. Less-Common Metals **6,** 283 (1964).

(Paper 70A2–393)

799–883 O-66—5