THE VAPOR PRESSURE OF THE METALS PLATINUM AND MOLYBDENUM.

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CONTINUING the line of investigation started by the determination of the vapor pressure of metallic tungsten,[1] the metals platinum and molybdenum have now been studied in a similar manner, and the results are given in this article.

The method involved is essentially the same as that described in the former paper, and consists in determining the loss of weight undergone by wires of the two metals maintained electrically at various temperatures for definite periods of time in glass vessels exhausted to an exceptionally good vacuum.

The calculation of the vapor pressure from the rate of loss of weight at a definite temperature is based upon the kinetic theory of gases and the Clausius-Clapeyron formula giving the relation between the vapor pressure of any substance and the temperature.

In the former paper the atomic heat of tungsten was assumed to be 6.8 at high temperatures. Recent work by Corbino and others, however, seems to indicate that the atomic heats of metals at temperatures as high as 2000° K., are considerably greater than would be expected according to the Dulong and Petit law. The most probable value for the atomic heats of platinum and molybdenum would therefore seem to be about 7.5 instead of the value 6.8 previously adopted. This gives, for the latent heat of evaporation of these metals,

$$(1) \qquad\qquad \lambda = \lambda_0 - 2.5\, T.$$

Following the method of the previous paper, we thus obtain:

$$(2) \qquad\qquad \log p = A - \frac{0.218\lambda_0}{T} - 1.26 \log T,$$

where A is a constant of integration, and

$$(3) \qquad\qquad \log m = A' - \frac{0.218\lambda_0}{T} - 1.76 \log T,$$

where

$$(3a) \qquad\qquad A' = A - \tfrac{1}{2} \log M/2\pi R,$$

[1] Phys. Rev., N. S., II., 329 (1913).

p = vapor pressure in dynes per sq. cm.,

m = rate of evaporation in grams per square centimeter per second,

M = atomic weight of the metal,

λ_0 = latent heat of vaporization at $0°$ K. in calories per gram atom,

R = gas constant $8.32.10^7$ ergs per degree,

T = absolute temperature (Kelvin).

The assumptions involved in these derivations are:

1. The "accommodation coefficient" of the vapor of the metal is unity. That is, every atom which strikes the metal surface is condensed, no reflection taking place.

2. The volume of the metal is entirely negligible when compared to the volume of the vapor, so that the Clausius-Clapeyron formula reduces to

$$\frac{d \ln p}{dT} = \frac{\lambda}{RT^2}.$$

3. The vapor of the metal is monatomic so that the specific heat of the vapor at constant pressure, is equal to $2.98 + R = 4.96$ calories per gram atom.

That the atoms of metal which evaporate from a hot wire are not reflected to any perceptible extent upon striking a surface, has been shown by many experiments in this laboratory. For example, if a single loop tungsten filament be heated in a highly exhausted bulb to such a temperature that the evaporation is fairly rapid, a dense black coating of the metal will be deposited uniformly over the glass. If, however, a screen, say of mica, be placed near the filament, that part of the bulb in the "shadow" of the obstruction will be perfectly clear with sharp boundaries. This shows that the atoms of tungsten travel in straight lines from the incandescent wire to the bulb, and that, at least from cold tungsten surfaces, the reflection of the tungsten atoms is negligible.

EXPERIMENTAL.

The molybdenum used was a sample of pure material made in this laboratory and consisted of wire 0.01549 cm. in diameter.

The platinum was obtained as wire 0.0254 cm. in diameter from Baker and Co., Newark, N. J. The temperature coefficient between $0°$–$100°$ C. was determined and found to be 0.0039 from $0°$ C. showing the material to be of the highest purity. Portions of this wire were drawn down to smaller sizes for the following experiments. The diameters ranging from 0.00572 to 0.0077 cm. were used.

The diameter of the molybdenum wire was measured carefully by a micrometer reading to 0.000025 cm.

The diameter of the platinum wire was calculated from the weight per centimeter using a density of 21.5. This is the more accurate way of obtaining the diameter, and would have been used with the molybdenum but the density of the latter is not so well known.

The general method of procedure was to mount a section of wire from 5 to 12 centimeters in length as a single loop on heavy nickel leading-in wires which was then sealed into a large straight sided lamp bulb about 9 cm. in diameter. The bulbs were carefully exhausted while heated to 360° C. by means of a mercury pump using liquid air to condense out water vapor and carbon dioxide. Before sealing off, the platinum or molybdenum filaments were heated electrically for about a minute to a bright red heat to drive off occluded gases and surface impurities. The bulbs were sealed off from the pump at a pressure of less than 0.001 mm. of mercury as read by a McLeod gage.

The wires were then set up to definite temperatures on the photometer bench, using the candle-power determination as the criterion of temperature as explained below, and maintained at constant temperature until the resistance had increased by from 5 to 10 per cent. The temperature was kept at the same value by maintaining the product of the voltage by the cube root of the amperes constant, this product being a function of the temperature only and independent of changing diameter.

After running in this way for a definite time, the bulb was opened, and the weight of the filament obtained and compared with the initial value. The final weight was the average weight per unit length found by weighing several pieces of the filament.

Weighings were made on a torsion balance reading directly to 0.01 milligrams.

The same formulas used in the paper on the vapor pressure of tungsten were used to calculate the rate of evaporation from the loss of weight and change in resistance. These are

$$(4) \qquad m = \sqrt{\frac{\rho}{\pi}} \frac{\sqrt{w_0} - \sqrt{w}}{t}$$

and

$$(5) \qquad m = \sqrt{\frac{\rho}{\pi}} \sqrt{w_0} \frac{1 - \sqrt{(R_0/R)}}{t},$$

where w_0 = original weight of the wire per unit length,

$\quad w$ = weight per unit length after the time t,

$\quad \rho$ = density of the wire,

$\quad r$ = radius of the wire,

$\quad R_0$ = initial resistance per unit length,

$\quad R$ = final resistance per unit length.

DETERMINATION OF TEMPERATURE.

The basis for the determination of the temperature of the wires was the same scale as used for tungsten in the preceding paper, modified by the ratio of the reflectivity of the metal in question to that of tungsten.

The temperature scale is based primarily on the following formula

$$T = \frac{11,230}{7.029 - \log H},$$

where H is the intrinsic brilliancy of the filament in international candle power per square centimeter of projected area. On this scale the melting point of tungsten is $3540°$ K.

In obtaining the candle power of the incandescent platinum and molybdenum, the wire was viewed through a calibrated slit, usually 2–4 cm. in width, which served the double purpose of cutting off light from that part of the filament cooled by the leads and of enabling an accurate determination of the length of the filament visible at the photometer head. Candle power per unit of projected area was thus readily obtained.

The emissivity of tungsten was taken as 0.514 and of molybdenum as 0.529[1], as compared to a black body. Hence in order to obtain the temperature from the curve of tungsten, the observed candle power for molybdenum was multiplied by the ratio 0.514/0.529.

The available published data on the emissivity for platinum varies so greatly, that a determination of the melting point was made as a check on the method. For this purpose three filaments of platinum, 0.0255 cm. in diameter, were carefully photometered, and quickly heated to the melting point and measurements of the volts, amperes and candle power were made at frequent intervals up to the burn-out point.

This method of obtaining the characteristics of a metal at its melting point has been found to be very reliable and reproducible in the case of tungsten, and the three measurements on platinum checked with each other within $5°$ C. The data obtained are as follows:

Bulb No.	Dia. Wire. Cm.	Length, Total. Cm.	Wire (Cm.), Visible.	Candle Power.	CP/ld
6,323–1	0.0255	19.0	10.50	4.46	16.6
6,323–2	0.0255	19.3	10.54	4.64	17.2
6,323–3	0.0255	18.6	10.56	4.54	16.9

Now the melting point of platinum is 1750–$1755°$ C.[2] and assuming

[1] H. v. Wartenberg, Ber. Dtsch. Phys. Ges. *12*, 105 (1910); W. W. Coblentz, Bull. Bureau of Standards, *7*, 198 (1911).

[2] Day & Sosman, Am. Journ. Sci., *29*, 161 (1910).

that we get within 5 degrees of the true melting point by the above method and taking the value 1750, we find the candle power per sq. centimeter at this temperature on the tungsten scale to be 30.2. The emissivity of platinum will then be equal to the product of the emissivity of tungsten 0.514 by the ratio of the candle powers 16.9/30.2, which is 0.288. This agrees quite closely with the value 0.278 determined by H. v. Wartenburg for block platinum.[1]

The temperatures of the three melting points as determined above are then 2022, 2027, and 2023 degrees Kelvin respectively if the value of 0.288 is taken for the emissivity.

RESULTS OF EXPERIMENTS.

The values of m, the rate of evaporation of the metal in grams per square centimeter per second, were calculated from the change in weight and also from the change in resistance by the formulas given above, and are tabulated in Table II.

TABLE II.

Rate of Evaporation of Platinum.

Identification Number.	Temp. of Wire °K.	$m \times 10^6$		$(1/T) \times 10^7$	Log m + 1.76 log T
		Weight.	Resistance.		
7,010–2	1,682	.00617	.0036	5,945	$\bar{3}$.470
6,916–3	1,710		.0052	5,848	
6,916–1	1,800	.0695	.049	5,555	$\bar{2}$.572
6,673–1	1,890	.373	.222	5,291	$\bar{1}$.332
7,010–3	1,912	.503	.363	5,230	$\bar{1}$.482
6,673–3	1,982	1.32	1.13	5,045	$\bar{1}$.921
6,673–5	2,000	1.88	1.35	5,000	.084

In order to determine whether m varied with the temperature according to the theoretical equation (3) the quantity log m + 1.76 log T was plotted against $1/T$.

According to equation (3) the points should lie along a straight line. Reference to Figs. 1 and 2 will show that the agreement is excellent in both cases.

The values of m determined by change in resistance are in every case lower than those found from the change in weight. This is due to the fact that the elimination of impurities from the metal by volatilization and a slow sintering process tend to decrease the specific resistance and so counteract the increase in resistance due to evaporation. While affecting the resistivity of the metal these impurities are present in such small traces that they introduce no appreciable error in the determination

[1] Ber. Dtsch. Physik. Ges., *12*, 105.

of loss of weight. Due to the low resistance of the heated wires, usually about 10 ohms, and the excessive cooling by the leading in wires, the values obtained from resistance measurements have been discarded in favor of these determined from change in weight. It will be noted however, that the quantities obtained by the two methods are not very different.

TABLE III.

Rate of Evaporation of Molybdenum.

Identification Number.	Temp. of Wire $^\circ K.$	$m \times 10^6$		$(1/T) \times 10^7$.	Log m + 1.76 log T.
		Weight.	Resistance.		
6,975–8	1994	.00766	.00635	5,015	$\overline{3}$.694
6,975–3	2040	.0305	.0286	4,902	$\overline{2}$.314
6,911–3	2056		.081	4,864	
6,911–2	2112	.124	.118	4,735	$\overline{2}$.953
6,975–5	2121	.111	.104	4,715	$\overline{2}$.905
6,430–2	2220	.630	.560	4,505	$\overline{1}$.689
6,911–1	2287	1.74	1.56	4,372	$\overline{0}$.150
6,430–1	2312	3.29	2.70	4,325	$\overline{0}$.447
6,975–2	2326	3.65	3.24	4,299	$\overline{0}$.492
6,430–3	2350	6.49	5.14	4,255	.742
6.975–1	2373	8.47	7.07	4,214	.868

From the slopes of the lines in Figs. 1 and 2 we obtain for platinum

$$0.218\lambda_0 = 27,800,$$

whence

$$\lambda_0 = 127,600 \text{ grams calories per mol};$$

and for molybdenum

$$0.218\lambda_0 = 38,600$$

whence

$$\lambda_0 = 177,000 \text{ gram calories per mol.}$$

From these values the heats of evaporation at any temperature are

Platinum............................ 127,600–2.5 T.
Molybdenum...................... 177,000–2.5 T.

The values of A', in equation (3) may also be calculated from Figures 1 and 2, the result being

Platinum............................ A 14.00
Molybdenum........................ A 17.110

Equation (3) thus becomes

$$\log m = 14.00 - (27800/T) - 1.76 \log T \qquad \text{for platinum,} \qquad (6)$$

and

$$\log m = 17.11 - (38600/T) - 1.76 \log T \qquad \text{for molybdenum.} \qquad (7)$$

From (3a) we can now calculate A, equation (2) becoming

$$\log p = 14.09 - (27800/T) - 1.26 \log T \qquad \text{for platinum} \qquad (8)$$

and

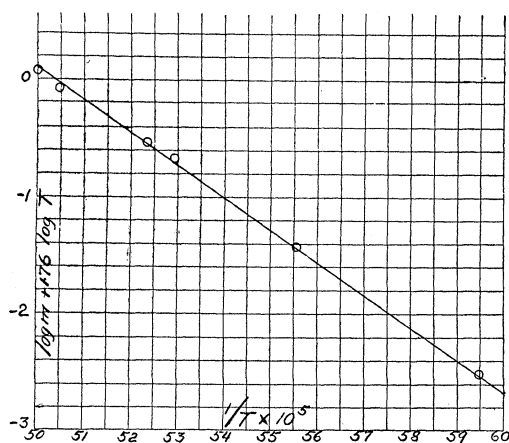$$\log p = 17.354 - (38600/T) - 1.26 \log T \qquad \text{for molybdenum.} \qquad (9)$$
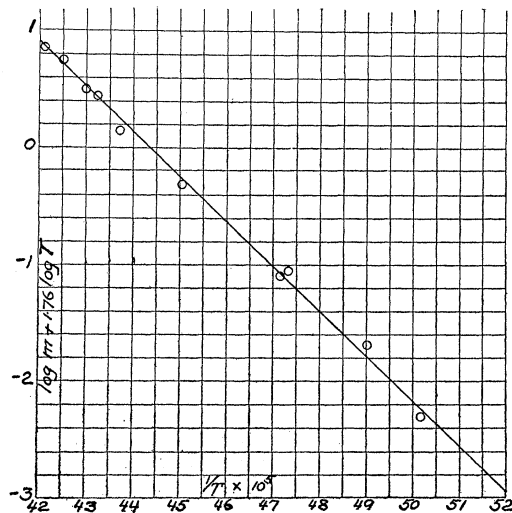

Fig. 1.

Rate of Evaporation of Platinum.

Fig. 2.

Rate of Evaporation of Molybdenum.

Since equations (6) and (7) represent the straight lines in Figs. 1 and 2, it is readily seen that this equation gives a very satisfactory method of calculating the rate of evaporation at any temperature.

Similarly, if it be assumed that the reflection of atoms of the metal is small, then equations (8) and (9) must give the vapor pressure with a fair degree of accuracy.

The rates of evaporation and vapor pressure at various temperatures as calculated from these equations is given in Tables IV. and V. Above the melting points, the vapor pressure would, of course, follow another curve. The boiling points calculated must therefore be looked upon as a lower limit. However, since the heat of fusion of metals is very small compared to their heats of vaporization the error is certainly not large, and it can therefore be safely concluded that the boiling points are in the neighborhood of the temperatures calculated.

TABLE IV.

Rate of Evaporation and Vapor Pressure of Platinum.

Absolute Temp.	Evaporation g per Sq. Cm. per Sec.		Vapor Pressure, Mm.	
1000	8.32	10^{-20}	324.0	10^{-20}
1050	161	10^{-20}	6415	10^{-20}
1100	.238	10^{-16}	9.70	10^{-16}
1150	2.75	10^{-16}	115	10^{-16}
1200	26.0	10^{-16}	1110	10^{-16}
1250	204	10^{-16}	8910	10^{-16}
1300	.137	10^{-12}	6.11	10^{-12}
1350	.791	10^{-12}	36.2	10^{-12}
1400	4.01	10^{-12}	188	10^{-12}
1450	18.5	10^{-12}	867	10^{-12}
1500	75.4	10^{-12}	3610	10^{-12}
1550	.279	10^{-9}	13.7	10^{-9}
1600	.966	10^{-9}	48.4	10^{-9}
1650	3.11	10^{-9}	156	10^{-9}
1700	9.06	10^{-9}	465	10^{-9}
1750	25.4	10^{-9}	1300	10^{-9}
1800	66.7	10^{-9}	3500	10^{-9}
1850	168	10^{-9}	8800	10^{-9}
1900	.397	10^{-6}	21.3	10^{-6}
1950	.920	10^{-6}	49.5	10^{-6}
2000	1.95	10^{-6}	107	10^{-6}
2028	2.97	10^{-6}	164	10^{-6}
4180			760 mm.	

CALCULATION OF THE VAPOR PRESSURE BY THE NERNST HEAT THEOREM.

According to Nernst's theorem, the vapor pressure of any substance is given approximately by the equation

$$(10) \qquad \log p = -\frac{\lambda_0}{4.571 T} + 1.75 \log T + C.$$

Here p is the pressure in atmospheres, λ_0 is the molecular heat of evaporation, and C is the chemical constant of the substance. Nernst finds for most substances that C has a value of about 3. If, then, we substitute $C = 3$, in the above equation, a roughly approximate relation between the vapor pressure and the heat of evaporation of a substance should be obtained.

Winterwitz[1] has shown that the previously published data on the vapor pressure of tungsten is in excellent agreement with such an equation.

It may be of interest, therefore, to compare the present data on platinum and molybdenum with the Nernst formula.

TABLE V.

Rate of Evaporation and Vapor Pressure of Molybdenum.

Absolute Temp.	Evaporation g per Sq. Cm. per Sec.		Vapor Pressure, Mm.	
1800	0.0863	10^{-9}	6.43	10^{-9}
1850	0.318	10^{-9}	23.5	10^{-9}
1900	1.057	10^{-9}	80.8	10^{-9}
1950	3.72	10^{-9}	288	10^{-9}
2000	10.0	10^{-9}	789	10^{-9}
2050	0.0283	10^{-6}	2.24	10^{-6}
2100	0.0763	10^{-6}	6.12	10^{-6}
2150	0.196	10^{-6}	15.9	10^{-6}
2200	0.480	10^{-6}	39.6	10^{-6}
2250	1.13	10^{-6}	94.1	10^{-6}
2300	2.57	10^{-6}	214	10^{-6}
2350	5.64	10^{-6}	479	10^{-6}
2400	12.0	10^{-6}	1027	10^{-6}
2450	.246	10^{-4}	21.4	10^{-4}
2500	.490	10^{-4}	43.0	10^{-4}
2550	.959	10^{-4}	85.0	10^{-4}
2600	1.791	10^{-4}	160	10^{-4}
2650	3.30	10^{-4}	298	10^{-4}
2700	5.95	10^{-4}	542	10^{-4}
2750	10.50	10^{-4}	918	10^{-4}
2800	18.1	10^{-4}	1679	10^{-4}
3890			760 mm.	

Let us calculate the value of C by (10) from the data on the vapor pressure of the three metals. Choosing a temperature in each case midway between the highest and lowest temperatures at which the rate of evaporation was measured, we obtain from the data of Table V. of the previous paper and from Tables IV. and V. of the present paper the following results:

[1] Physik. Zeit., *15*, 397 (1914).

TABLE VI.

	T	p Mm.	p Atmos.	λ_0	C
W.........	2,700	6.9×10^{-6}	9.1×10^{-9}	218,000	3.5
Pt.........	1,850	8.8×10^{-6}	11.6×10^{-9}	128,000	1.5
Mo........	2,200	$40 \ \times 10^{-6}$	53.6×10^{-9}	177,000	4.4

The chemical constant C in the last column was calculated from equation (10) by substituting in it the above values of T, p, and λ_0.

The value of C for platinum is unusually low, whereas that of molybdenum is considerably higher than the value 3.0 given by Nernst for the average of a large number of substances.

If, instead of calculating C, we assume it to be equal to 3.0 for each metal, and then choose a value of λ_0 which will give the best agreement with the experiments, we obtain

for   W, $\lambda_0 = 210,000,$

Pt, $\lambda_0 = 136,000,$

Mo, $\lambda_0 = 162,000,$

instead of the values given in Table VI.

In view of the merely approximate form of the Nernst equation used, it is difficult to decide what weight should be given to the above results.

SUMMARY.

1. The rates of evaporation of heated platinum and molybdenum wires in high vacuum were determined over rather wide ranges of temperature.

2. From these data the vapor pressures of these metals were calculated. The results are given in equations (6) to (9) and in Tables II. to V.

The latent heat of vaporization of these metals (in calories per gram atom) is found to be:

Pt, $128000 - 2.5\ T,$

Mo, $177000 - 2.5\ T.$

These results are found to be in moderately good agreement with an approximate equation derived by Nernst.