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THE VAPOR PRESSURE OF METALLIC TUNGSTEN.[1]

By Irving Langmuir.

THE vapor pressure of metals has been the subject of many investigations in recent years.

Greenwood[2] has directly determined the boiling points of several metals at three or four different pressures. The method adopted was to heat the metal in a carbon or magnesia crucible in an electric furnace and to observe the temperature at which drops of metal were first thrown up from the molten surface. The metals studied were copper, tin, silver, lead, bismuth, antimony, magnesium, iron, chromium, manganese, and aluminum. The boiling points at atmospheric pressure ranged from 1120° C. for magnesium to 2450° for iron.

Recently von Wartenburg[3] has determined quantitatively the vapor pressures of lead, silver, and thallium by the dynamical method, that is, by passing an inert gas very slowly over the heated metal and measuring the concentration of the metal vapor in the gas.

The volatility of many metals has been qualitatively observed, but except in the case of the metals given above and such easily volatile metals as mercury, zinc, and the alkali and alkaline earth metals there are no quantitative determinations of the vapor pressures or boiling points known to the writer.

The volatility of the materials used for filaments of incandescent lamps is the principal factor determining the useful life of such lamps.

Experiments were therefore undertaken to determine the rate of evaporation of tungsten in vacuum at various temperatures up to the melting point.

The kinetic theory enables us to calculate the vapor pressure from this

[1] A preliminary statement of the results of this investigation has appeared in the Journal of the Amer. Chem. Soc., *35*, 931, 1913.

[2] Chem. News, *104*, 31–33, 42–45, 1912.

[3] Z. f. Electrochem., *19*, 482, 1913.

rate of evaporation, or at least to obtain a lower limit for the vapor pressure.

RELATION BETWEEN VAPOR PRESSURE AND RATE OF EVAPORATION IN A VACUUM.

Let us consider a surface of metal in equilibrium with its saturated vapor. According to the kinetic theory we look upon the equilibrium as a balance between the rate of evaporation and the rate of condensation. That is, we conceive of these two processes going on simultaneously at equal rates.

In the case of liquids or solids at temperatures near their boiling points or even at temperatures so low that their vapor pressures are in the neighborhood of one millimeter, we are accustomed to consider that there must always be equilibrium between the vapor and the liquid or solid at the surface between the two. For example, no matter how rapidly we may boil water we are probably justified in considering that the steam is saturated at the surface boundary between the water and the steam.

This, however, simply means that when we boil water as rapidly as we can, the net rate at which steam is produced is very small compared to the actual rate at which the water is evaporating into steam and the steam again condensing on the water.

At much lower temperatures, where the vapor pressure is of the order of magnitude of .001 mm. the rate of evaporation of a substance even in a practically perfect vacuum is very small. This is not due to the cooling of the substance by its own evaporation, but simply to the fact that the rate at which the molecules of vapor are formed is limited.

For example, we cannot make mercury freeze by placing it in a very high vacuum, although we know it has a perceptible vapor pressure even at its freezing point.

At temperatures so low that the vapor pressure of a substance does not exceed a millimeter, we may consider that the actual rate of evaporation of a substance is independent of the presence of vapor around it. That is, the rate of evaporation in a high vacuum is the same as the rate of evaporation in presence of saturated vapor. Similarly we may consider that the rate of condensation is determined only by the pressure of the vapor.

Now the rate at which the saturated vapor comes into contact with the metal may be readily calculated from the principles of the kinetic theory when the vapor pressure is known. Certainly the rate of condensation of the vapor cannot exceed the rate with which it comes into contact with the solid or liquid.

This calculation is similar to that of the effusion of gases through small openings.[1]

Let us consider a unit cube of the vapor one side of which is bounded by the metal. We will calculate the rate at which the vapor comes into contact with the metal. Half of the molecules in this unit volume are moving towards the metal, and the other half are moving away from it. If we let ρ be the density of the gas, then the mass of gas moving toward the metal is $\frac{1}{2}\rho$.

Let Ω be the average (arithmetical) velocity of the molecules. It can be readily shown that the average *component* of the velocity in any given direction is then $\frac{1}{2}\Omega$. Hence the average velocity with which the gas molecules in the mass $\frac{1}{2}\rho$ are *approaching* the metal is $\frac{1}{2}\Omega$. The mass of gas (m) which strikes against the unit surface of metal per second is therefore $\frac{1}{2}\rho \times \frac{1}{2}\Omega$, thus

$$m = \tfrac{1}{4}\rho\Omega. \tag{1}$$

The ordinary gas law $pV = RT$ may be written

$$\rho = \frac{pM}{RT}, \tag{2}$$

where p = pressure,
M = molecular weight,
T = absolute temperature (° Kelvin),
R = gas constant = 83.2×10^6 ergs per degree.

The average velocity (Ω) of the molecules is given by the relation

$$p = \frac{\pi}{8}\rho\Omega^2, \tag{3}$$

whence from (2)

$$\Omega = \sqrt{\frac{8RT}{\pi M}}. \tag{4}$$

Substituting (2) and (4) in (1) we get for the rate at which the vapor comes into contact with the metal

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p. \tag{5}^2$$

If we can assume that every atom of the vapor which strikes the metal condenses, then the equation (5) gives the desired relation between the vapor pressure and the rate of evaporation in vacuo. If, however, a certain proportion (r) of the atoms of the vapor is reflected from the surface then the vapor pressure will be greater than that calculated from (5) in the ratio $1 : (1 - r)$.

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[1] Cf. Meyer's Kinetic Theory of Gas, German edition, 1899, p. 82.

[2] This equation has been previously used by the author in calculating the velocity of reaction between oxygen and tungsten. Jour. Amer. Chem. Soc., *35*, 106, 1912.

There are good reasons for believing that the reflection of vapor molecules from the surface takes place to a negligible degree only. Knudsen[1] has shown from measurements of the heat conductivity of gases at low pressures that the number of molecules of a gas which are reflected from a smooth surface (*i. e.*, do not reach thermal equilibrium with the surface) is as much as 70 per cent. in the case of hydrogen but very much less with gases of higher molecular weight. Knudsen gives the name accommodation coefficient to the quantity $1 - r$. He finds for example

Gas.	Surface.	Accommodation Coefficient.
H_2	Polished platinum	0.36
CO_2	Polished platinum	0.87
H_2	Platinized platinum	0.71
CO_2	Platinized platinum	0.98

Timiriazeff[2] finds the accommodation coefficient to have significance in determining the "slip" of gases in viscosity measurements at low pressure.

The accommodation coefficient for a vapor with such high molecular weight as that of tungsten would probably be nearly unity for any kind of surface. There is every reason to believe, moreover, that the accommodation coefficient would be particularly high in the case of a metal and its own saturated vapor. It is extremely probable therefore that equation (5) gives a very close approximation to the true vapor pressure.

Knudsen[3] has determined the vapor pressure of mercury at temperatures from 0° to 50° by a method involving the use of an equation similar to (5). He used a relatively large surface of mercury, however, and allowed the saturated vapor thus obtained to escape through a small opening into a space practically free from mercury vapor. From the rate of escape of the mercury he calculated the pressure of the vapor by an equation equivalent to (5). This method differs in principle from that employed for the present determination of the vapor pressure of tungsten only in having an opening through which the vapor diffuses instead of having the vapor simply diffuse out through the surface of the metal itself. Knudsen's method has the advantage that his results are practically unaffected by any possible reflection of the vapor molecules from the surface, but it has the disadvantage that is cannot be directly applied to determining the vapor pressures of such difficultly volatile substances as tungsten.

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[1] Ann. Phys., *34*, 593, 1911.

[2] Ann. Phys., *40*, 971, 1913.

[3] Ann. Physik., *29*, 179, 1909.

Variation of the Rate of Evaporation with the Temperature.

The relation between the vapor pressure of any substance and the temperature is given by the Clausius-Clapeyron formula.

$$\lambda = T\frac{dp}{dT}(v - v_0). \tag{6}$$

In the case of tungsten the volume of the metal is entirely negligible as compared to the volume of the vapor, so we may place $v_0 = 0$. If we consider λ to be the latent heat of evaporation per mol of tungsten (184 grams) then since $pv = RT$ we have

$$\frac{d\ln p}{dT} = \frac{\lambda}{RT^2}. \tag{7}$$

This result could have been obtained directly from Van't Hoff's equation.

In general λ is a function of the temperature such that

$$\frac{d\lambda}{dT} = C_v - C_s, \tag{8}$$

here C_v is the specific heat (per mol) of the vapor (at constant pressure), and C_s is the specific heat per mol of the solid metal.

We may safely consider tungsten vapor to be monatomic[1] and hence its specific heat at constant pressure is

$$C_v = 2.98 + R = 4.96 \text{ calories per gram atom.} \tag{9}$$

The atomic heat of solid tungsten is given as 6.3 by Gin (1908) and as 7.8 by Corbino.[2] The higher value is rather improbable, so that the best value would seem to be about

$$C_s = 6.8. \tag{10}$$

Substituting (9) and (10) in (8) and integrating we have:

$$\lambda = \lambda_0 - 1.8T. \tag{11}$$

This result substituted in (7) and integrated gives, after changing from natural to common logarithms:

$$\log p = A - \frac{0.218\lambda_0}{T} - 0.9 \log T, \tag{12}$$

where A is a constant of integration.

Taking the logarithm of equation (5) we obtain

$$\log m = \log p + \tfrac{1}{2}\log\frac{M}{2\pi R} - \tfrac{1}{2}\log T. \tag{13}$$

Combining this with (12):

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[1] Langmuir, Jour. Amer. Chem. Soc., *35*, 944, 1913.

[2] Phys. Zeitsch., *13*, 375, 1912.

$$\log m = A' - \frac{0.218\lambda_0}{T} - 1.4 \log T, \tag{14}$$

where

$$A' = A + \tfrac{1}{2} \log \frac{M}{2\pi R}. \tag{15}$$

Equation (14) gives us the rate of evaporation of tungsten as a function of the temperature. There are two empirical constants A' and λ_0 to be determined from the experiments.

EXPERIMENTS ON THE RATE OF EVAPORATION OF TUNGSTEN IN VACUUM.

Several sets of experiments were made to determine the rate of evaporation. In each case lamps were made up with tungsten filaments, and the filaments were heated for various times at various temperatures. The rate of evaporation was determined usually by both of two methods, namely by increase in resistance and by decrease in weight.

First Set.—Five tungsten lamps were made up with single loop filaments without supports. The length of the wire used ranged from 10.6 to 11.2 cm. and the diameter was .0162 cm. These lamps were set up on life test at an efficiency of one watt per maximum horizontal candle power and maintained at constant voltage. The initial candle power varied from 40 to 41 among the various lamps. These lamps were taken off test after 500 to 1,000 hours, broken open, and the filaments weighed.

Second Set.—Five lamps similar to the last with lengths of filament from 10.6 to 11.2, and of the same diameter as before were set up on test at 0.8 watt per maximum horizontal candle power and maintained at constant voltage. The initial candle powers ranged from 58.5 to 60.5. These lamps were taken off test after 200 to 300 hours, and the filaments were weighed.

Third Set.—Two lamps containing single loop filaments of wire .0122 cm. diam. were made up. The filament of the first was 11.1 cm. long. This lamp was set up at constant voltage at an original temperature of 2800° K. (determined by color). The readings taken at frequent intervals were:

TABLE I.

Time, Minutes.	Volts.	Amperes.	Candle Power.
0	23.6	2.94	164
14	23.6	2.93	—
21	23.6	2.93	153
56	23.6	2.89	124
72	23.6	2.88	112

The second lamp had a filament 14.3 cm. long. This lamp was set up by color at 3136° K. and kept at constant voltage. The characteristics were:

TABLE II.

Time, Minutes.	Volts.	Amperes.	Candle Power.
0	35.5	3.55	504
1	35.5	——	311
2	35.5	3.38	238
3	35.5	3.30	199

Fourth Set.—This set was made up at a later date than the previous ones, and the measurements were conducted with much greater care. Five lamps were made up from wire .00709 cm. diameter, each with a length of about 77 cm. mounted in six loops. These lamps were photometered and set up with the filaments at temperatures ranging from 2738 to 2925° K.

The voltage was adjusted at frequent intervals so as to keep the product $V\sqrt[3]{A}$ constant. (V = volts, A = amperes.) In this way, notwithstanding a considerable change in the diameter of the filament, the temperature is maintained constant. This is readily seen from the following reasoning. The energy radiated is proportional to the diameter whence the function VA/d (watts divided by the diameter) is a function of the temperature but not of the diameter. Similarly if the material of the wire is unaltered, the resistance is inversely proportional to the square of the diameter, hence Vd^2/A is a function of the temperature but not of the diameter. Therefore

$$\frac{V^2A^2}{d^2} \times \frac{Vd^2}{A} = V^3A$$

is a function of the temperature but not of the diameter. Hence if $V\sqrt[3]{A}$ is maintained constant the temperature must remain constant even when the diameter changes.

The weight of the wire before sealing into the lamps was found to be 0.764 mg. per cm. of length.

The lamps were run as follows:

TABLE III.

No.	Temp.	Initial Volts.	Initial Amps.	Time, Minutes.	Final Volts.	Final Amps.	Final Wt. Mg per Cm.
1	2738	195	1.182	233	198	1.129	
2	2825	208	1.240	111	213	1.157	0.676
3	2875	216	1.260	65	222	1.159	0.671
4	2925	230	1.310	40	238	1.184	0.656
5	2930	235	1.318	14.5	237	1.269	0,722

The temperatures were determined by comparison of the color of the light emitted from the filament with that of a standard lamp viewed through a special blue glass. The details of this method of estimating temperatures will be given in a subsequent paper. For the present it will suffice to say that the temperature scale is primarily based on the following formula

$$T = \frac{11,230}{7.029 - \log H}. \tag{16}$$

Here H is the intrinsic brilliancy of the filament in international candle power per sq. cm. (projected area). On this scale the melting point of tungsten is 3540° K.

The initial volts and amperes give the characteristics of the lamps as first set up (after two hours ageing of the filament at 2400° K.).

The final volts and amperes give the characteristics after being set up at the indicated temperature for the time given in the fourth column.

The final weight is the average weight per unit length as found by weighing several lengths of the filament on a delicate microbalance after breaking open the bulbs.

Calculation of the Rate of Evaporation.

Let w_0 = the original weight of the wire per unit length,
w = the weight per unit length after the time t,
ρ = the density of the wire,
r = radius of the wire,
R_0 = its initial resistance per unit length,
R = its final resistance per unit length.

Then it is easily seen that

$$w = \pi r^2 \rho,$$

or

$$r = \sqrt{\frac{w}{\pi\rho}}. \tag{17}$$

Now the effect of the evaporation is to remove tungsten from the surface at a rate proportional to the extent of the surface. That is, the thickness removed per unit time is constant and equal to m/ρ. Therefore

$$\frac{m}{\rho} = \frac{r_0 - r}{t} = \frac{\sqrt{w_0} - \sqrt{w}}{t} \frac{1}{\sqrt{\pi\rho}}, \tag{18}$$

whence

$$m = \sqrt{\frac{\rho}{\pi}} \cdot \frac{\sqrt{w_0} - \sqrt{w}}{t}. \tag{19}$$

This equation gives the rate of evaporation m in terms of the density and weight per unit of length of the filament.

Since the resistance is inversely proportional to the cross-section we have

$$\frac{R_0}{R} = \frac{w}{w_0}. \tag{20}$$

Substituting this in (19) gives

$$m = \sqrt{\frac{\rho}{\pi}}\sqrt{w_0} \cdot \frac{1 - \sqrt{\dfrac{R_0}{R}}}{t}, \tag{21}$$

from which m can be calculated from the changes in resistance.

It should be noted, however, that (20) assumes that the specific resistance remains unaltered, therefore equation (21) applies only when the filament is kept at constant temperature, as for example in the fourth set of experiments. In the first three sets of experiments, on the other hand, the lamps were run at constant voltage. The temperature therefore gradually decreases, and for this reason the resistance does not increase as rapidly as if the filament were kept at constant temperature. From data on the characteristics of tungsten filaments available in this laboratory it has been calculated that at constant voltage a 1 per cent. decrease in current corresponds to a decrease in cross-section of 1.11 per cent. or an increase of 1.11 per cent. in resistance at constant temperature. Therefore, before applying equation (21) to the data in the first three sets of experiments an 11 per cent. correction should be made in the changes in the resistance that are produced by the evaporation.

In calculating m from equations (19) or (21) the value of ρ was taken to be 19.4 which gives for $\sqrt{\rho/\pi}$ the value 2.486 in gram cm. units.

In calculating the values of m from the data of the fourth set of experiments, the values of $\sqrt{R_0/R}$ were plotted as a function of t and the best representative straight line was drawn among them. The slope of this line was used to calculate m according to equation (21).

Results of Experiments.

The values of m, *i. e.*, the rate of evaporation of tungsten in grams per sq. cm. per second, were calculated by equations (19) and (21) as described above, and are tabulated below (Table IV.).

In order to determine whether m, the rate of evaporation, varies with the temperature according to the theoretical equation (14) the quantity $\log m + 1.4 \log T$ (column VI.) was plotted (Fig. 1) against $1/T$ (column V.).

According to equation (14) the points should lie along a straight line. Reference to Fig. 1 will show that the agreement is excellent, although the values of m vary in the ratio 1 : 15,000.

TABLE IV.

I. Set.	II. Lamp.	III. Temp. of Fil. °K.	IV. $m \times 10^6$.	V. $\frac{1}{T} \times 10^6$.	VI. log m + 14 log T.	VII. Method.
I.	—	2440	0.0020	409.8	6.05–10	Weight.
II.	—	2522	0.0059	396.5	6.53–10	"
III.	1	2800	0.39	357.1	8.42–10	Resistance.
"	2	3136	30.	318.9	0.38——	"
IV.	1	2738	0.151	365.2	7.99–10	"
"	2	2825	0.52	354.0	8.54–10	"
"	2	2825	0.59	354.0	8.59–10	Weight.
"	3	2875	1.01	347.8	8.84–10	Resistance.
"	3	2875	1.14	347.8	8.90–10	Weight.
"	4	2925	1.73	341.9	9.10–10	Resistance.
"	4	2925	2.33	341.9	9.23–10	Weight.
"	5	2930	1.84	341.3	9.13–10	Resistance.
"	5	2930	2.45	341.3	9.25–10	Weight.

The values of *m* determined by the 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 traces of impurities from the tungsten by volatilization and a slow sintering process tend to decrease the specific resistance of the tungsten and hence counteract the increase in resistance due to evaporation. In fact, in the first and second sets of experiments at 2440 and 2520° respectively, the resistance during the first part of the life actually *decreased*, so that the resistance measurements are totally unreliable as a source of information about the rate of evaporation. At higher temperatures, however, these changes in specific resistance take place much more rapidly than at lower temperatures, and the resistance measurements become of greater significance.

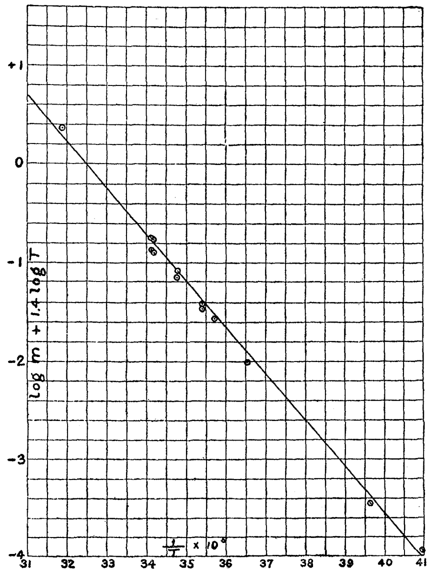

Fig. 1.

The values of *m* found from the changes in resistance are therefore probably not as accurate as those found from the loss of weight, but nevertheless serve as a very valuable check on the latter.

From the slope of the straight line in Fig. 1 we obtain

$$0.218\lambda_0 = 47{,}440,$$

whence

$$\lambda_0 = 217{,}800 \cdot g\text{—calories per mol.}$$

From this by (11) the heat of evaporation of tungsten at any temperature is $\lambda = 217{,}800 - 1.8T$.

We can also calculate the value of A', equation (14), from Fig. 1. We obtain

$$A' = 15.402.$$

Equation (14) thus becomes

$$\log m = 15.402 - \frac{47{,}440}{T} - 1.4 \log T. \tag{22}$$

From (15) we can now calculate A; equation (12) thus becomes

$$\log p = 15.502 - \frac{47{,}440}{T} - 0.9 \log T. \tag{23}$$

Since equation (22) represents the straight line on Fig. 1, it is readily seen that this equation gives a very satisfactory method of calculating the rate of evaporation at any temperature.

Similarly, if we may assume that the reflection of tungsten atoms from solid tungsten is small, then equation (23) must give the vapor pressure with a fair degree of accuracy.

In Table V. are given the rate of evaporation, and the vapor pressure of tungsten at various temperatures as calculated from equations (22)

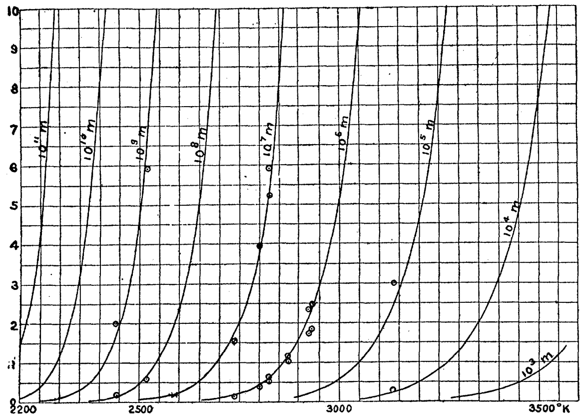

Fig. 2.

Rate of evaporation of tungsten in a vacuum (m = grams of tungsten per square cm. per sec.). Points experimentally determined (see Table IV.); curves calculated from equation (22).

TABLE V.

Rate of Evaporation and Vapor Pressure of Tungsten.

Absolute Temp.	Evaporation g per sq. cm. per sec.	Vapor Pressure, mm.
2000° K.	114. $\times10^{-15}$	6.45 $\times10^{-12}$
2100	1.44 $\times10^{-12}$	83.2 $\times10^{-12}$
2200	14.4 $\times10^{-12}$	849. $\times10^{-12}$
2300	116.7 $\times10^{-12}$	7.05 $\times10^{-9}$
2400	798. $\times10^{-12}$	49.2 $\times10^{-9}$
2500	4.67 $\times10^{-9}$	294. $\times10^{-9}$
2600	23.6 $\times10^{-9}$	1.51 $\times10^{-6}$
2700	106. $\times10^{-9}$	6.95 $\times10^{-6}$
2800	429. $\times10^{-9}$	28.6 $\times10^{-6}$
2900	1.57 $\times10^{-6}$	106. $\times10^{-6}$
3000	5.23 $\times10^{-6}$	0.000362
3100	16.3 $\times10^{-6}$	0.00114
3200	46.7 $\times10^{-6}$	0.00333
3300	126. $\times10^{-6}$	0.00910
3400	320. $\times10^{-6}$	0.0234
3500	769. $\times10^{-6}$	0.0572
(3540)	.00107	0.080
(5110)	——	760.

and (23). Above the melting point of tungsten the vapor pressure would follow another curve. The boiling point 5110° calculated from equation (23) 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 point of tungsten must lie in the neighborhood of 5100° K.

The data in Table V. have been plotted in Figs. 2 and 3. In Fig. 2 the rates of evaporation as determined by experiment (Table IV.) are plotted. It is seen that the equation (22) fits in well with the observations.

SUMMARY.

1. It is shown that the vapor pressure (p) of a substance is related to its rate of evaporation (m) in a vacuum by the following relation:

$$m = \sqrt{\frac{M}{2\pi RT}}\,p,$$

where M is the molecular weight of the vapor. In the derivation of this equation it is assumed that all the molecules of vapor which strike the surface of the metal are condensed (not reflected). No other assumptions except those that have received ample experimental verification need be made.

2. Experiments were made to determine the rate of evaporation of tungsten in a vacuum at temperatures ranging from 2440° K. up to 3136° K. Over this temperature interval of 700° the rate of evaporation increased in the ratio 1 : 15,000.

3. From these data the vapor pressures were calculated and were found to agree excellently with the thermodynamical relations such as the Clausius-Clapeyron formula. The latent heat of evaporation of solid tungsten is thus found to be (per 184 grams)

$$\lambda = 217{,}800 - 1.8T \text{ calories,}$$

a value higher than the heat evolved by any known chemical reaction.

4. The rate of evaporation of tungsten at any temperature in a perfect vacuum is given accurately by the equation

$$\log_{10} m = 15.402 - \frac{47{,}440}{T} - 1.4 \log_{10} T;$$

here m is the rate of evaporation in grams per sq. cm. per second.

5. The vapor pressure of tungsten in mm. of mercury at the absolute temperature T is given by the equation

$$\log_{10} p = 15.502 - \frac{47{,}440}{T} - 0.9 \log_{10} T.$$

6. The vapor pressure of tungsten at 2400° K. the temperature of the filament in a lamp running at 1 watt per candle, is about 50×10^{-9} mm.

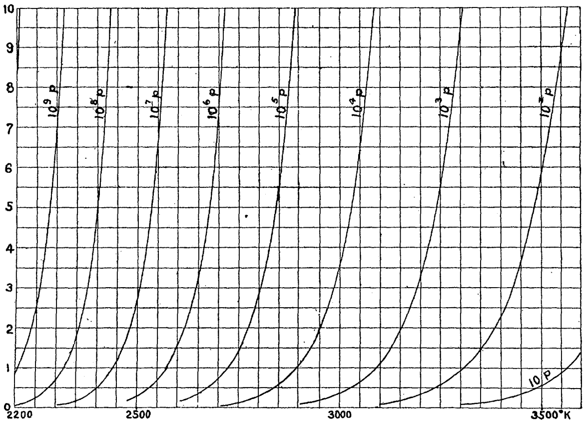

Fig. 3.
Vapor pressure of tungsten in millimeters of mercury.

At the melting point of tungsten, 3540° K., the vapor pressure is 0.080 mm. The boiling point of tungsten at atmospheric pressure is probably very close to 5100° K. The vapor pressure at other temperatures is given in Table V.

7. The rate of evaporation and the vapor pressure of tungsten are given in Table V. Curves of the same data are given in Figs. 2 and 3.

In subsequent papers the writer intends to publish data on the rates of evaporation and vapor pressures of platinum, carbon, molybdenum, tantallum, osmium, and some of the commoner metals such as copper, silver, nickel, and iron.

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