

EVAPORATION OF TUNGSTEN UNDER VARIOUS PRESSURES OF ARGON

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ABSTRACT

Theory of the mechanism of the evaporation of a tungsten filament in the presence of an inert gas.—A theory of the evaporation of a heated tungsten filament immersed in an inert gas is developed in which it is assumed that the evaporating atoms diffuse through a film of stationary gas surrounding the filament. The diameter of the film is calculated from Langmuir's equation for the heat loss from a filament. The theory leads to the relation $maP \log b/a = \text{constant}$, where m is the rate of evaporation, P is the pressure, and a and b are the diameters of the filaments and gas film respectively.

Test of the theory. Rate of evaporation of a tungsten filament at 2870°K in a gas mixture, 86% argon, 14% nitrogen.—By measuring the loss in weight of the filament the rate of evaporation for various gas pressures was calculated. The rates varied from 230×10^{-9} gr/cm² sec. in a vacuum to 2×10^{-9} gr/cm² sec. at a pressure of 165 cm. It is shown that when b is calculated from Langmuir's equation for heat loss the expression $maP \log b/a$ is actually constant for gas pressures in excess of 10 cm. The fact that the round filaments developed a hexagonal cross-section in accord with the normal crystalline shapes of tungsten grains is further evidence of the backward diffusion of evaporated metal with consequent condensation on the filament.

IN A paper published several years ago¹ the author described experiments on the rate of evaporation of tungsten filaments. These filaments varied in crystalline structure and in diameter. At constant temperature the former of these factors was found to be of marked influence both in vacuum and in the inert gases, argon and nitrogen, and the diameter was found to be of no influence in vacuum—results which were in accord with accepted hypotheses of evaporation.

In the case of the inert gases, however, a surprising feature developed, in that the diameter of the filament was found to be a noteworthy factor. The larger the diameter, the smaller proved to be the rate of evaporation. This result was explained quantitatively by the assumption that the evaporation from a filament in a gas at a pressure near atmospheric is a diffusion phenomenon within a certain limited range of distance from the filament's surface. In his theory for the heat loss from incandescent wires in gases, Langmuir has conceived² that the filament is surrounded by a stationary cylindrical film of gas through which the heat from the filament is carried purely by conduction. The assumption of the existence of such a film of the same dimension was found to be also useful in explaining the mechanism of evaporation. The filament was considered to be surrounded by tungsten

¹ G. R. Fonda, Phys. Rev. **21**, 343 (1923).

² I. Langmuir, Phys. Rev. **34**, 406 (1912).

vapor at the same pressure as would be present in a vacuum. The atoms of this vapor, however, instead of being projected directly from the filament, as in a vacuum, were pictured as diffusing through the stationary film of gas. Once an atom reached the outer boundary of the film, it would be carried away in the convection current of gas and would be lost to the filament; but the path within the film was so irregular that an atom might in fact return to the filament and be deposited on it, thus leading to a reduced evaporation as compared with that in a vacuum.

The results of the tests at constant pressure of gas and temperature of filament were found to fit the empirical expression, $m a \log b/a = \text{constant}$, where m is the rate of evaporation from the filament, a the diameter of the filament, and b the diameter of the gas film, calculated from the Langmuir equation.

As the filament increases in diameter, the value of b likewise increases somewhat. For such a case the expression is in accord with a decrease in the rate of evaporation, and it is obvious that an increase in either a or b should increase the chance of an irregularly diffusing atom of tungsten colliding once more with the filament.

Another test of this hypothesis is to vary the pressure of gas and note whether the expression still remains constant. In this case the diameter of the stationary gas film increases as the pressure is diminished—a change favoring a still lower rate of evaporation by allowing a greater chance for the return of evaporated atoms to the filament. This however is more than counteracted by the fewer collisions between tungsten atoms and molecules of gas—a change which allows of a more ready and direct diffusion of the former through the film of gas. The present experiments have been made in various pressures of argon to test the validity of this hypothesis. The course of the diffusion in such a case can be derived as follows and an expression obtained similar to the empirical one already described.

For the diffusion of tungsten atoms through a gas, $dq/ds = D dc/dr$, where dq is the number of atoms passing through area ds , dc/dr is the concentration gradient of tungsten atoms in a direction at right angles to ds , and D is the diffusion coefficient in the gas. If this diffusion is uniformly distributed over the area s , $q = Dsdc/dr$, or, for the diffusion from a wire through an area of surrounding gas having unit length,

$$q = D 2 \pi r dc/dr. \quad (1)$$

The Meyer formula for the diffusion of two gases,³ expressed in terms of the atoms of tungsten vapor (W) and the molecules of argon gas (A) involved here, is

$$D = (1/3n)(u_W l_W n_A + u_A l_A n_W)$$

where u is the root mean square velocity, l the mean free path, and n the number of molecules per cc.

³ Meyer, *Kinetische Theorie der Gase*, 1895, Art. 95.

At a constant filament temperature of 2870°K, at which the tests were made, n_w is negligibly small (corresponding to a pressure of 0.000017 mm),⁴ compared with n_A , so that n , the total number of molecules per cc, is virtually equal to n_A , and the second term falls out, giving the expression $D = (1/3)u_w l_w$.

The velocity of tungsten atoms is a function of filament temperature and is therefore likewise constant in these tests.

As the mean free path of the tungsten atoms is dependent on the pressure of the argon, their coefficient of diffusion is inversely proportional to the pressure P and Eq. (1) becomes $q = (2\pi r/P)dc/dr$, and this integrated gives

$$(1/2\pi) \int dr/r = dc/qP.$$

For wire of diameter a and gas film of diameter b , calculated as before from the Langmuir equation for heat loss,

$$(1/2\pi) \int_{b/2}^{a/2} dr/r = (1/2\pi) \log b/a.$$

Furthermore if m is the rate of evaporation per unit of surface, $q/2\pi a$, then

$$maP \log b/a = \int dc = c_a - c_b = \text{constant} \quad (2)$$

where c_a and c_b are the concentrations of the tungsten atoms at the surface of the filament and at the surface of the gas film, respectively. These concentrations are constant because in a case like this, where the filament burns at a constant temperature in argon at various pressures, it is assumed that the diffusion of tungsten atoms is the only variable and that the concentration of tungsten vapor is constant at the outer border of the gas film, regardless of the pressure, just as it is at the surface of the filament, where it is determined of course by the vapor pressure. These assumptions are borne out by the experiments.

In the experiments the filaments were of a constant diameter of 0.00978 cm and bent into a hairpin shape, having a total length of 12 cm. They were all set up initially at a constant temperature, as determined by color match, of 2870°K on the Worthing and Forsythe temperature scale⁵, and were then burned at constant voltage. The rate of evaporation was determined from the loss in weight and was calculated from Langmuir's equation⁶

$$m = (\rho/\pi)^{1/2} (w_i^{1/2} - w_f^{1/2})/t$$

where ρ is the density of tungsten, 19.3; w_i and w_f are the initial and final weights of the filament in gr/cm; and t is the time in seconds.

⁴ Jones, Langmuir and Mackay, Phys. Rev. **30**, 211 (1927).

⁵ Worthing and Forsythe, Astrophys. J. **61**, 146 (1925).

⁶ Langmuir, Phys. Rev. **2**, 329 (1913).

The gas used was a mixture of 86% argon and 14% nitrogen, such as is used at present in gas-filled lamps. It was introduced to the lamps at various pressures, as noted in the table. The values recorded are the averages of several tests made at different times, all in good agreement with one another. Each test was itself an average taken from measurements of six lamps which had been treated simultaneously.

A pressure of two atmospheres was attained by having a supplementary bulb attached to the lamps and sealing both off as a unit at a pressure of 700 mm. The lamp was then immersed in liquid air to condense some of the

TABLE I
Rate of evaporation of tungsten in 86% argon, 14% nitrogen at 2370°K.
Diameter of filament = 0.00978 cm.

Press (cm)	Rate Evap. $m(10)^9$	b (cm)	$maP \log b/a \times 10^9$	$m/b \times 10^9$
0	230	—	—	—
1	57.5	9.68	3.9	—
5	23.5	2.42	6.3	—
10	20.5	1.31	9.8	15.6
25	10.3	0.63	10.4	16.2
50	5.4	0.36	9.6	14.8
70	4.2	0.28	9.6	14.8
165	2.0	0.15	8.8	13.5

mixture and the supplementary bulb sealed off. Examination of the gas in the latter allowed of determination of the pressure in the lamp. This operation led of course to a slight enrichment of the argon in the lamp, amounting to about 3%, sufficient to reduce the rate of evaporation 1.5%. Allowance is made for this in the table, so that all values recorded are for the one composition of 86% argon.

These values are plotted on the curve of Fig. 1. They hold only for wire of this specific diameter, because, as already noted, filaments of a larger size have lower rates of evaporation in gas.

In the case of the tests in vacuum, the value found experimentally of $230 (10)^{-9}$ is in good agreement with that of $250 (10)^{-9}$, as given by Jones, Langmuir and Mackay.⁴

The expression $maP \log b/a$ is sufficiently constant at pressures above 10 cm to allow of credence being given the hypothesis developed above.

The constancy of the expression has a further significance, for, as is evident from its derivation, it denotes a constant difference between the vapor pressure of tungsten at the surface of the filament and at the surface of the film of gas. For constant filament temperature this implies that the concentration of tungsten vapor at the surface of the stationary film of gas should be constant for all pressures above 10 cm. It is this vapor which constitutes that which effectively evaporates from the filament, for the rising convection currents of gas carry it off to be deposited on the bulb. The rate of evaporation at different pressures should be determined therefore by the area of the assumed film of gas if the concentration of vapor at its border is

in fact a constant. As a criterion of this, values of m/b are given in the last column of the table. It is evident that this expression is sufficiently constant for pressures of 10 cm and above to render the hypothesis credible.

The rate of evaporation in 86% argon 14% nitrogen at 50 cm pressure is 2.3% of that in vacuum at the temperature of 2870°K and for this size of wire. Other experiments have shown that at 2720°K it is a still smaller percentage of the rate in vacuum—in other words, the vapor pressure of tungsten at the boundary of the film of stationary gas is smaller proportionately to the vapor pressure at the filament surface. More of the tungsten evaporating evidently returns to the filament as its temperature is reduced, no doubt because of the greater density gradient of the argon.

For pressures below 10 cm the hypothesis developed above breaks down for obvious reasons, as the diameter of the stationary film of gas becomes

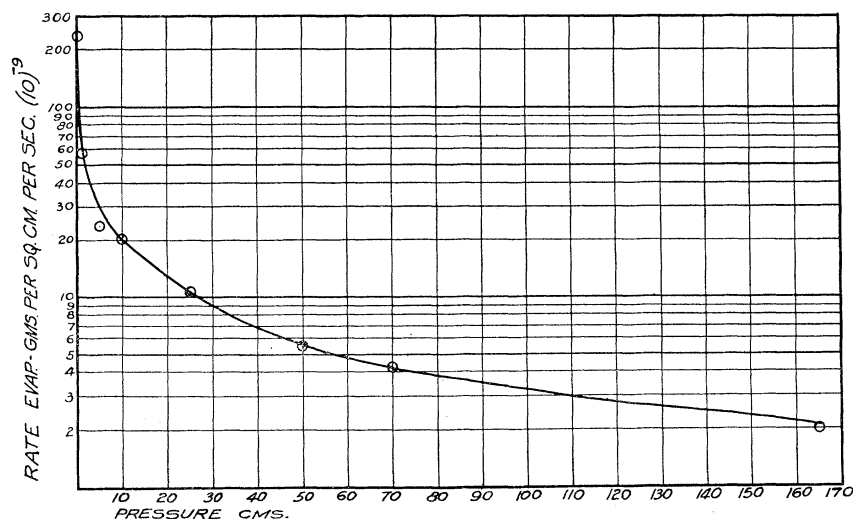


Fig. 1. Rate of evaporation of tungsten in a gas mixture, 86% argon, 14% nitrogen for various gas pressures. Temperature of filament 2870°K, diameter of filament 0.00978 cm.

greater than that of the bulb. Another relationship quite evidently should hold here. One has been developed by Weber⁷ and applied to experiments by Oosterhuis which calls for proportionality between the rate of evaporation and the square root of the gas pressure. Although it does not hold as well at higher pressures as the expression developed above, it gives such agreement at the range of low pressures as to warrant consideration for expressing the mechanism of evaporation in cases where there are no convection currents of gas.

The appearance of the filaments bore testimony to the assumption that the evaporation from them had been a diffusion phenomenon. They had all

⁷ Weber, *Handelingen van het XVI Nederlandsch. Natuur en Geneeskundig Congres*, 1917, p. 102.

been taken from the same spool of non-sag tungsten wire, which has the characteristic of developing long grains in the process of grain growth accompanying heating of the wire. When tested in a vacuum this wire was found to remain uniformly round throughout its life. The filaments tested in gas, however, were found to have become approximately hexagonal in cross-section. The hexagonal cross-section was more perfectly developed at the lower temperature of 2720°K, where, as already shown, deposition is still more marked.

Such filaments are similar in appearance to those single crystals of tungsten described by vanArkel⁸ which he had prepared by heating a single crystal of tungsten in the presence of tungsten hexachloride vapor. The latter was decomposed and its tungsten content deposited on the filament, but in such a manner that the originally round filament became coated with a deposit whose cross-section was hexagonal.

In the case of the experiments described herein on filaments heated in argon, there has evidently been a similar action, except that the deposit, instead of coming from an extraneous source, is made up of atoms which have been carried away from the filament by evaporation and have then returned to it again by the process of diffusion. In this return those atoms which adjust their position to the orientation of the crystal on which they fall are more strongly held than those whose orientation is different. The latter therefore evaporate again more readily and the result is the formation of a cross-section in accord with the normal crystalline structure of the metal. As Langmuir says in a discussion of what he terms "reversible sublimation," in accounting for the ability of condensing atoms to arrange themselves to form a crystalline unit:⁹ "The continual evaporation and condensation going on over the whole surface of the crystal allow the atoms to arrange themselves in the most stable position."

This mechanism explains satisfactorily the change from a round to an hexagonal cross-section without the necessity of assuming that it is due to a difference in vapor pressure on the different faces. In fact, when a filament prepared by the vanArkel process was tested in vacuum at a temperature of 2720°K until it had lost about 30% in weight and failed by burn-out, its cross-section was still hexagonal, with the angles between faces just as sharp as initially.

These data on the variation in rate of evaporation with pressure of argon are of value in calculating the lives of gas-filled lamps. The other factor involved is the heat loss through the gas which determines the temperature of operation. The fact that the rate of evaporation increases for pressures below atmospheric does not necessarily mean that the life of lamps at constant efficiency decreases correspondingly. If the effective diameter of the filament is so small that the heat loss is relatively large, then a reduction in pressure may so decidedly lower the heat loss and consequently the operating

⁸ van Arkel, *Physica* **3**, 76 (1923).

⁹ I. Langmuir, *Jour. Amer. Chem. Soc.* **38**, 2253 (1916).

temperature that the rate of evaporation will actually be reduced. Such a condition existed in the early low wattage lamps whose filament was of such sagging wire that it had to be wound on a small mandrel to retain its shape during operation. For such a lamp a maximum life was calculated for a pressure of one-half atmosphere and was confirmed by test. With the advent of non-sag wire, the filaments of gas-filled lamps could be given such large effective diameters that both calculation and test are in agreement in showing a continuous increase in life with increase in pressure for all sizes of lamps.

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