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Effect of Argon Pressure on the Sublimation Rate of Magnesium

Z. Ogorelec

*Institute of Physics, Faculty of Science and Institute »Ruđer Bošković«,
Zagreb, Croatia, Yugoslavia*

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The sublimation rate of magnesium in an argon atmosphere with pressures ranging from 10^{-6} up to 760 mm Hg was measured. At pressures from 10^{-6} to 10^{-2} mm Hg the sublimation rate is approximately constant. It considerably decreases at higher pressures. At pressures of about 10^2 mm Hg the sublimation rate of magnesium is very low. As the transfer of vapour from the surface of the sample to the condenser takes place by diffusion at higher pressures and by molecular flow at lower pressures, it is not possible to treat the problem uniformly. The results of the present experiments are therefore related to some approximative equations.

INTRODUCTION

The rate of sublimation is a quantity of great importance in making use of sublimation under reduced pressure. It depends on the properties of the substance and its temperature, but also on the pressure of the residual gases. Since the dependence on the pressure in the range from zero to a few hundred mm Hg can be mathematically expressed only in an approximate way, the actual change of sublimation rate with pressure will usually be determined by experiment.

At first, the object of such experiments was the rate of evaporation. G. R. Fonda¹ and I. Langmuir² examined the evaporation rate of tungsten in a mixture of argon and nitrogen as used in gas-filled lamps. The empirical data on the change of evaporation rate of zinc with pressure of the residual gases were given by M. Spendlove³.

The rate of distillation was also studied under various pressures, and results for some organic substances were published as a comprehensive review by K. C. D. Hickman⁴. The present paper describes a study of the influence of argon pressure on the sublimation rate of magnesium under conditions required for its purification by fractional sublimation.

EXPERIMENTAL

A sample shaped into a thin-walled tube was put into a Pyrex vessel which in turn was placed into a heater having a temperature of $T = 878^\circ\text{K}$. As the temperature decreases from one end to the other, magnesium was condensed in the same vessel but nearer to its open end. The mass of sublimated magnesium was determined by weighing the residual magnesium in A and the sublimated magnesium in B (Fig. 1). During the process of sublimation a small quantity of magnesium reacts with the glass, which introduces an error in the weighing. The loss of magnesium in A, as the weighing shows, is nearly the same as the weight of sublimated magnesium in B. It may be concluded from this that the error due to

chemical reaction of magnesium with glass is small in comparison with the errors due to variation of temperature. The samples were prepared from three times resublimated high purity magnesium and thanks to the shape of the sample the change of its surface during the sublimation process can be neglected.

The duration of the process was measured from the moment when the vessel with the sample was placed into the heater to the moment when the vessel was removed out of it. It was supposed that the same quantity of magnesium sublimated during the warming of the sample to the working temperature and during its cooling off.

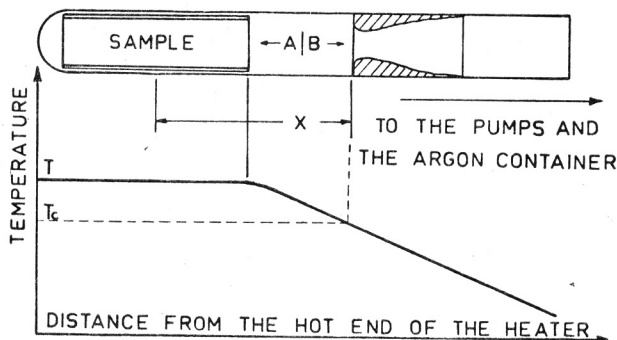


Fig. 1. Temperature along the pyrex tube with the sample.

The temperature was controlled by a Pt-PtRh thermocouple. Oxygen was removed from the argon gas used in the experiment by passing it over copper scrapings at 500°C and then drying it over silicagel. Argon pressure was controlled by a Penning and a thermocouple gauge at lower pressures and by a mechanical gauge at higher ones.

The rate of sublimation is obtained by dividing the total quantity of sublimed magnesium by time and by the area of the sample. Results of measurements are shown in Fig. 2.

DISCUSSION

The sublimation or distillation rate is defined as the number or the mass of molecules transported from a given surface and deposited on a condenser in the unity of time. The presence of gases or vapours above the metal affects the rate of sublimation in two distinct ways. Due to collisions between evaporating molecules part of them will be returned to the surface of the sample, and thereby the total number of metal molecules which escape from the solid phase will be reduced. The inert atmosphere above the sample reduces the transfer of vapour, even when the inert-gas pressure is low. This influence becomes negligible only at pressures at which the mean free path of the evaporated molecules in the gas is much larger than the distance from sample to the surface where molecules condense.

When sublimation takes place from a flat surface to a stagnant atmosphere under pressure P , and when the vapour condenses on a flat and parallel condenser at a distance X , the transfer of vapour is accomplished only by diffusion and the rate of sublimation is given by

$$w = \frac{MDP}{RTX} \ln \frac{P - P_c}{P - P_i} \quad (1)$$

- where D = diffusion constant of the vapour
 M = molecular weight of the vapour
 R = gas constant
 T = sample temperature in $^{\circ}\text{K}$
 P_i = partial pressure of the vapour at the sample surface
 P_c = saturation vapour pressure at the condenser temperature T_c

Equation (1) is valid only in the presence of an atmosphere. If the space above the sample is free from gases, the transfer of vapour is not governed by dif-

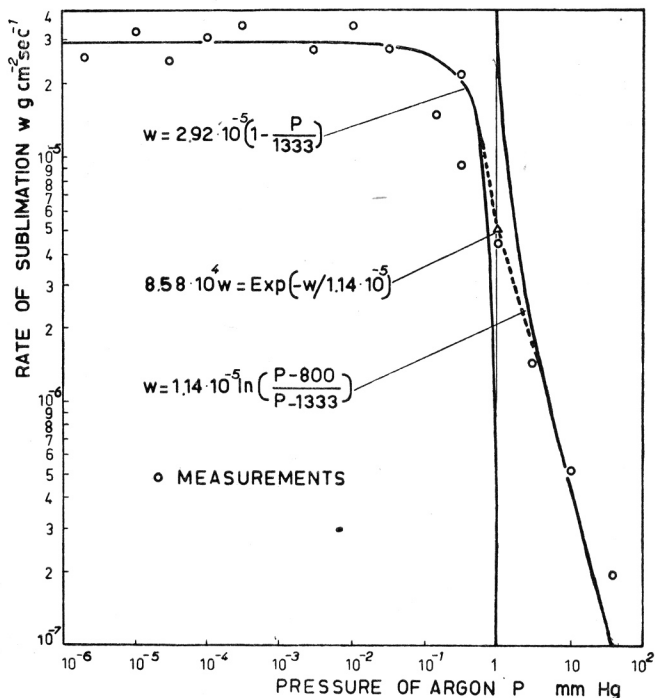


Fig. 2. Plots of equations (7) and (8) and the experimental points.

fusion, and the rate of sublimation depends only on properties of the sample and its temperature. The kinetic theory gives

$$w = w_0 \left(1 - \frac{P_i}{p} \right) \tag{2}$$

where p is the saturation vapour pressure at temperature T , and w_0 is the absolute rate of evaporation given by $w_0 = fp \sqrt{M/2\pi RT}$, where f is the coefficient of evaporation defined by G. Burrows⁵.

Equations (1) and (2) are useful under certain conditions. Thus, equation (1) gives the real values of w only if $P > P_i$. From equation (2) the rate of sublimation can be calculated also for $P \neq 0$, where the mean free path of evaporating molecules is much larger than the distance between the surface of evaporation and the surface of condensation. In order to fit the experimental

data with the above relations it is necessary to correct equations (1) and (2). According to Carman⁶, for pressures $P > p$, the rate of sublimation can be expressed by the equation

$$w = \frac{MDP}{RTX} \ln \frac{P - P_c}{P - p}, \quad (3)$$

and for pressure $P < p$ by

$$w = w_0 \left(1 - \frac{P}{p} \right) \quad (4)$$

In the range of pressures where $P \approx p$, equations (1) and (2) must give the same results for w . We now have

$$w_0 \left(1 - \frac{P_i}{p} \right) = \frac{MDP}{RTX} \ln \frac{P - P_c}{P - P_i} \quad (5)$$

The data⁶ for the distillation of water and the sublimation of ice are in good agreement with the above equations, and the following calculations show that Carman's approximation is also useful in treating the sublimation rate of magnesium, because the experimental conditions allow such a treatment.

As the surface of the sample and the condenser are neither flat, nor parallel and equal in area, equation (3) is valid only if its right side is multiplied by a correcting factor β . The diffusion constant D is unknown, but it depends on pressure and temperature according to $D = \gamma P^{-1} T^{3/2}$. If the product $\beta \cdot \gamma$ is denoted by δ we have

$$w = \delta \frac{M \sqrt{T}}{RX} \ln \frac{P - P_c}{P - p} \quad (6)$$

The experiment gives $T = 878^\circ\text{K}$, $M = 24.32 \text{ g mol}^{-1}$, $X = 3 \text{ cm}$, $P_c = 0.6 \text{ mm Hg} = 800 \text{ din cm}^{-2}$, $p = 1 \text{ mm Hg} = 1333 \text{ din cm}^{-2}$ and the comparison of equation (6) with results of measurements shows that $\delta = 3.95$. Equation (6) is now

$$w = 1.14 \times 10^{-5} \ln \frac{P - 800}{P - 1333} \quad \text{for } P > 1 \text{ mm Hg} \quad (7)$$

Carman in his calculations assumed that at $P = 0$ all molecules had been removed from the space above the sample *i.e.* $P_i = 0$. Thus at $P = 0$ the evaporation rate is w_0 . In our case for $P = 0$ the partial vapour pressure $P_i \neq 0$ and the rate of evaporation is not w_0 , but $w_m = \epsilon w_0$. It is therefore plausible to write equation (4) in the form

$$w = w_m \left(1 - \frac{P}{p} \right)$$

As the experiment gives for w_m the value $2.92 \times 10^{-5} \text{ g cm}^{-2} \text{ sec}^{-1}$ this equation assumes the numerical form

$$w = 2.92 \times 10^{-5} \left(1 - \frac{P}{1333} \right) \quad \text{for } P < 1 \text{ mm Hg} \quad (8)$$

The relations (7) and (8) are graphically compared with the experimental points in Fig. 2.

In the range where $P \approx p$ the rate of sublimation is calculated for $P = p = 1$ mm Hg. By eliminating the partial vapour pressure P_i from (5) and using the experimental data one obtains

$$8.58 \times 10^4 w = \exp \left(- \frac{w}{1.14 \cdot 10^{-5}} \right) \text{ for } P = p = 1 \text{ mm Hg} \quad (9)$$

The graphical solution of this equation gives $w = 5.16 \times 10^{-6} \text{ g cm}^{-2} \text{ sec}^{-1}$, which is in good agreement with the measurements. As the value of the absolute rate of evaporation w_0 in our experiment was $9.71 \times 10^{-3} \text{ g cm}^{-2} \text{ sec}^{-1}$ (it is assumed that $f = 1$), the factor ε will be very small viz. $\varepsilon = 0.003$. This is caused by rather unfavourable geometrical conditions.

Consequently, the present experiment shows that the change of the sublimation rate of magnesium can be described by simple equations for a particular case. However, it is possible to treat in the same way the change of the sublimation rate of other metals and for a different inert atmosphere.

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IZVOD

Utjecaj tlaka argona na brzinu sublimacije magnezija

Z. Ogorelec

Mjerena je brzina sublimacije magnezija u atmosferi argona pod tlakovima od 10^{-6} do 760 mm Hg. Rezultati mjerenja pokazuju da je brzina sublimacije približno konstantna do tlaka od 10^{-2} mm Hg, a zatim se naglo smanjuje. Kod tlakova reda veličine 10^2 mm Hg brzina sublimacije poprima vrlo male vrijednosti. Budući da se transport para s površine uzorka vrši kod viših tlakova difuzijom, a kod nižih strujanjem molekula, nije moguće eksperimentalne rezultate interpretirati u cijelom području tlakova na isti način. Eksperiment je zato tumačen pomoću nekih aproksimativnih relacija.

FIZIČKI ZAVOD

PRIRODOSLOVNO-MATEMATIČKI FAKULTET

I

INSTITUT »RUĐER BOŠKOVIĆ«
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