

## VAPORIZATION UNDER THE INFLUENCE OF AN ELECTRIC FIELD

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### ABSTRACT

The thermodynamic equilibrium of a system solid gas in a non-uniform electric field is computed. The results as applied to a cylindrical metal filament in a radial field in an enclosure of uniform temperature  $T$  are as follows: (1) The density of the saturated vapor is given by  $n_r = n_0 e^{-(\beta/kT)(1/r_0^2 - 1/r^2)}$  at a radius  $r$ ,  $\beta$  being a function of the electric moment, the polarizability of the atoms and of the field applied. (2) The heat of evaporation of the substance of the filament is increased by  $\Delta\phi = \frac{\beta}{r_0^2}$  being the radius of the filament. (3) The apparent rate of evaporation is to the normal rate in the ratio  $e^{-(\beta/kT)(1/r_0^2 - 1/r^2)}$ . The surface effects have been neglected. Comparing the result 3 with experiments, (the only one for which we have experimental data) it is found that this theory does not represent all that is happening.

### I. INTRODUCTION

**M**OLECULES are known to be built up of movable electric charges, electrons, and protons, the orbits of which may be deformed by an external electric field. The centers of gravity of the positive and the negative charges are displaced from their original position by the field. The result of this displacement is a polarization, or in other words the production of an electric moment.

Molecules can be divided into two classes according to the presence or absence of a permanent electric moment, that is, according to the separation or the coincidence of the two centers of gravity in the absence of an external field. The molecules which do possess a permanent moment are called dipoles.

If a field is applied to a gas we should expect the following effects: (a) an orientation of the dipole molecules, (b) a polarization of all molecules, (c) a translation of all molecules in the direction of the field. All these effects correspond to certain changes in potential energy of the molecules.

This paper is the result of a study of the effect of an electric field upon the evaporation of solids. Such a phenomenon depends directly on the potential energy of the molecules. Qualitatively speaking, the following effects are possible: an increase in the heat of evaporation because of the added potential energy of the molecules; a non-homogeneous distribution of the molecules in the container as the electric field will tend to move them; a vapor pressure changing with position in the volume as the molecules are accelerated in given directions by the external field; an effect upon the rate of evaporation; and finally a different behavior as regards the temperature for the dipole in comparison with the non-dipole molecules.

The general procedure followed in calculating these effects is classical. We first compute the thermodynamic probability  $w$  and, by investigating its maximum, we obtain the conditions of equilibrium giving us the number of molecules in the gaseous state.

## II. THERMODYNAMIC PROBABILITY

As is well known the thermodynamic probability can be divided into two parts: one containing the external field, and another without it, according to the equation

$$W_1 = W_0 \int e^{-\chi/kT} dq_1 dq_2 \dots \quad (1)$$

where  $W_0$  is the probability without field,  $\chi$  the potential energy of the system due to the external field, and the  $q$ 's are the coordinates of the molecules, the integration being extended over the volume of the container.

By the Boltzmann theorem

$$W_0 = C \int e^{-(E_g + E_s)/kT} d\tau \quad (2)$$

where  $C$  is a constant,  $E_g$  is the energy of the gas consisting of  $n$  molecules,  $E_s$  is the energy of  $n'$  molecules of the solid. Introducing the known expressions for  $E_g$  and  $E_s$  in Eq. (2), and integrating over all elements of volume  $d\tau$  of the phase space we obtain<sup>1</sup>

$$W_0 = C e^{-n\phi_0/kT} V_g (2\pi m kT)^{3n/2} (2\pi A kT)^n (kT/\nu_a)^{3n'} \quad (3)$$

where  $\phi_0$  is the heat of vaporization per molecule at the absolute zero,  $V_g$  is the volume occupied by the gas and  $\nu_a$  is the geometrical mean of the frequencies of the  $n'$  molecules of the solid, these molecules being considered as oscillators;  $A$  is the moment of inertia of the molecule.

The potential energy  $E_p$  is the work done by bringing a molecule from the surface of the solid into the space of the gas against the non-uniform electric field. Then

$$E_p = - \int \mathbf{S} ds \quad (4)$$

where  $\mathbf{S}$  is force acting on the molecule which is given by

$$\mathbf{S} = (\mathbf{u} \mathbf{r}_1) \nabla (d\psi/dr) \quad (5)$$

where  $\psi$  is the potential from which the field arises,  $\mathbf{r}_1$  is a unit vector in the direction of the gradient of the field,  $\mu$  is the total electric moment that is

$$\mathbf{u} = \mathbf{u}_1 + \alpha \nabla \psi \quad (5a)$$

where  $\mathbf{u}_1$  is the permanent moment of a molecule,  $\alpha \nabla \psi$  the moment induced by the field due to the polarizability  $\alpha$  of a molecule. Hence

$$E_p = - \int_{s_0}^s (\mathbf{u} \mathbf{r}_1) \nabla (d\psi/dr) ds \quad (6)$$

In order to calculate this energy we must assume a definite form for the potential  $\psi$ . Let us consider then the evaporating solid in the form of a

<sup>1</sup> Born, Atom Theorie des poten Zustandes, p. 704.

cylindrical rod of radius  $r_0$ . Surrounding the first cylinder we will take another of radius  $r_e$  which shall represent the boundary of the volume. A difference of potential is applied to these cylinders. It produces a non-uniform field in the space between them. This particular type of apparatus was chosen because it is easy to realize experimentally.<sup>2</sup>

The potential is then given by

$$\psi = -2\eta \log r + C \quad (7)$$

where  $\eta$  is the electric charge per unit length of the cylinder.

We may now proceed to evaluate the energy of position of a molecule. From Eqs. (5a) and (6) we have

$$E_p = - \int_{r_0}^s [\mu_1 \cos_a \theta + \alpha \nabla \psi] \nabla(d\psi/dr) ds \quad (8)$$

Here  $\cos_a \theta$  is the average value of  $\cos \theta$ . On account of the thermal agitation, the angle  $\theta$  between  $\mu_1$  and the field intensity varies continuously; but a certain equilibrium will be established between the orienting influence of the field and the deorienting influence of the thermal motion. Thus we can speak of the time average of  $\cos \theta$ . It has been calculated by Debye, who obtained

$$\cos_a \theta = (\mu_1/3kT) \nabla \psi$$

Thus with Eq. (7) and the above value Eq. (8) becomes

$$E_p = (\mu_1^2/3kT + \alpha) 2\eta^2 (1/r_0^2 - 1/r^2) \quad (9)$$

considering that  $\chi = \Sigma E_p$  we can now use Eqs. (3) and (9) in Eq. (1) and calculate the probability

$$\begin{aligned} W_1 &= \frac{W_0}{V_0^n} \int \exp \left[ -\frac{1}{kT} \sum \left( \frac{\mu_1}{3kT} + \alpha \right) 2\eta^2 \left( \frac{1}{r_0^2} - \frac{1}{r^2} \right) \right] \Pi dv \\ &= W_0 e^{-\beta n/kTr_0^2} \end{aligned} \quad (10)$$

Where

$$\beta = (\mu_1^2/3kT + \alpha) 2\eta^2 \quad (10a)$$

Eq. (10) gives us the number of complexions in the general phase space. Each complexion is realized by any one of the possible distributions of  $n$  gaseous and  $n'$  solid molecules. Thus in order to find the probability  $W$  that  $n$  molecules, of the total number  $N = n + n'$  are in the gaseous state and  $n'$  in the solid state, we must multiply  $W_1$  by the number of possible distributions of  $N$  molecules in two groups of  $n$  and  $n'$  molecules respectively,<sup>1</sup> and by the number of possible arrangements of the  $n'$  molecules of the solid, that is by

$$N!n'/n!n'! = N!/n!$$

Thus by Eq. (10) we have

$$W = (N!/n!) W_0 e^{-\beta n/kTr_0^2} \quad (11)$$

<sup>2</sup> A. G. Worthing, Phys. Rev. 17, 418 (1921).

The stationary state is characterized by the maximum of  $W$  or  $\log W$ , i.e.

$$d \log W / dn = 0$$

which gives for  $n$  the value

$$n = V_g \frac{(2\pi)^{5/2} m^{3/2} A}{k^{1/2} T^{1/2}} \nu^3 \exp \left[ -\frac{\phi_0}{kT} - \frac{\beta}{kT r_0^2} \right] \quad (12)$$

The expression (12) gives us the number of gaseous molecules present in the volume  $V_g$  as a function of the temperature and of the electric field. We see that the effect of the field is analogous to an increase of the heat of vaporization per molecule amounting to

$$\Delta\phi = (\mu_1^2 / 3kT + \alpha)(2\eta^2 / r_0^2) \quad (13)$$

The behavior of a dipole gas in contrast to that of a gas, the molecules of which have no permanent electric moment, is clearly seen in the appearance of the temperature in Eq. (13).

### III. DISTRIBUTION OF MOLECULAR DENSITY

The number of molecules present in a certain element of volume is obviously proportional to the probability of a molecule being in this element. If we call  $n_0$  the molecular density at a point in the immediate neighborhood of the solid rod the molecular density at any other point will then be given by

$$n_r = n_0 e^{-E_p / kT} \quad (14)$$

In order to determine  $n_0$  we make use of the fact that the total number of molecules must be given by Eq. (12)

$$n = \int n_r dr = n_0 \int e^{-E_p / kT} dv$$

from which we obtain

$$n_0 = \frac{(2\pi)^{5/2} m^{3/2} A}{k^{1/2} T^{1/2}} \nu^3 e^{-\phi_0 / kT} \quad (15)$$

which shows that the molecular density is unchanged in the neighborhood of the rod by the presence of the external field. This is quite obvious as the potential energy of the molecules in this position is the same whether the field is present or not. If we combine Eqs. (15) and (14) we see how the molecular density decreases as we move away from the evaporation rod.

### IV. RATE OF EVAPORATION

The rate of evaporation is defined as the number of molecules emitted into a vacuum per unit surface of the evaporating body per unit of time. When an evaporating body is in equilibrium with its vapor the number of molecules emitted per unit time is just equal to the number of molecules which condense back on the body as it is this condition which determines the stationary state. Thus if we can calculate the number of molecules which

strike the surface of the evaporating body (assuming that each collision results in a condensation)<sup>3</sup> when the pressure is equal to the saturated vapor pressure, we will have the rate of evaporation.

The evaporation and the condensation are two independent phenomena, one does not affect the other; the rate of evaporation in absence of a field depends upon the temperature alone. Let us assume that the temperature is high enough to give such a vapor pressure that the mean free path is very small compared to the dimensions of the apparatus. Then the rate of condensation is entirely conditioned by the molecular density in the immediate neighborhood of the evaporating surface for as we have said, it depends upon the number of molecules striking the surface, a number which in turn is proportional to the number of molecules per unit volume. This we have seen in Eq. (15) is unaffected by the electric field and thus we find that at high molecular densities the rate of evaporation remains the same whether an electric field is present or not.

If now the cylinder enclosing the evaporating material is permeable to the molecules the conditions will be somewhat different. This case is easily realized experimentally by replacing the cylinder surrounding the evaporating rod by a grid or spiral to which the electric field can be applied. In vacuum and in the absence of field the molecules move undisturbed in the direction of their initial velocity until a collision takes place. With the field, however, the molecules escaping from the rod will be retarded in their motion and only those having a definite initial velocity will reach the permeable cylinder and fly into the space outside in which no field is present, and where we shall assume that they condense. Now the rate of evaporation should be given by the number of molecules condensing outside as the phenomenon takes place in vacuum; however, as some molecules *will* be brought back to the solid by the external field this measured rate of evaporation will be different from that we discussed above. This can be illustrated by a simple calculation.

Call  $dn_x$  the number of molecules per unit volume of the solid having an  $x$  component of velocity between  $U$  and  $U+dU$ . Then

$$dn_x = \text{constant} \times e^{-mU^2/2kT} dU.$$

Of these molecules only such as have a kinetic energy sufficient to balance the potential energy of evaporation  $\phi_0$  will escape from the rod and of these only the molecules having an additional energy  $\beta(1/r_0^2 - 1/r^2)$  will reach a point  $r$  in the field. Therefore all the molecules having a kinetic energy  $L \equiv \phi_0 + 2\beta\eta^2(1/r_0^2 - 1/r_e^2)$  or a velocity

$$u \equiv [(2/m) \{ \phi_0 + 2\beta\eta^2(1/r_0^2 - 1/r_e^2) \}]^{1/2}$$

will escape and condense outside of the cylinder. Then the number of molecules escaping in a unit time is

$$n_f = \text{constant} \times \frac{kT}{m} \exp \left[ -\frac{\phi_0 + \beta(1/r_0^2 - 1/r_e^2)}{kT} \right]$$

<sup>3</sup> Langmuir, Phys. Rev. **2**, 336 (1913).

If now we put  $\beta=0$  we obtain the number  $n_0$  of molecules that would escape if no field were present. For the ratio of the two we find

$$\frac{n_f}{n_0} = \exp \left[ -\frac{\beta}{kT} \left( \frac{1}{r_0^2} - \frac{1}{r_e^2} \right) \right] \quad (16)$$

This last result is quite important from an experimental point of view as we shall see in the next paragraph.

#### V. NUMERICAL VALUES AND DISCUSSION OF AVAILABLE DATA

The values of  $\mu_1$  and  $\alpha$  have been determined for quite a number of substances by previous investigators. As is well known  $\mu_1$  is most readily computed from the variation of the dielectric constant with the temperature. As regards  $\alpha$  the last named experiments can also yield its value but a much easier procedure is to derive it from the data on index of refraction and molecular refraction.

The numerical values of these two constants vary for the different substances but they are of the following order of magnitude (which alone interests us for the present)

$$\alpha \sim 10^{-24} \text{ cm}^3 \epsilon; \quad \mu_1 \sim 10^{-18} \text{ e. s. u.}$$

In all our expressions  $\alpha$  and  $\mu_1$  enter in the form of the function defined in Eq. (10a). We shall thus calculate  $\beta$  assuming  $T$  to be 1000. The Boltzmann constant  $K$  has the value  $1.37 \times 10^{-16}$  ergs degree<sup>-1</sup>. Then

$$\mu_1^2/3kT + \alpha \approx 10^{-24} \epsilon \text{ cm}^3$$

As an average value of  $\phi_0$  we shall take  $10^{-12}$  ergs and compare it with its increase (13) due to the external field. Let us assume a rod of radius 0.001 cm as the evaporating body and take for instance the radius of the outer cylinder to be 0.5 cm. The potential difference between the two electrodes will be taken as 30,000 volts. These conditions are approximately satisfied by the experiments of Worthing<sup>2</sup> on the evaporation of tungsten in an electric field. The charge per unit length of the condenser then becomes by Eq. (7)

$$\eta \approx 8 \text{ e. s. u.}$$

The field strengths at the surface of the filament is by Eq.  $4.8 \times 10^6$  volts/cm and finally  $\Delta\phi$  (13) becomes approximately  $10^{-15}$  ergs per molecule which is a thousand times smaller than  $\phi_0$ . Thus under these favorable conditions the contribution of the electric field to the latent heat of evaporation is negligible.

If we now compare the rates of evaporation we shall find quite a different result. As a matter of fact (16) gives us the ratio of the two rates, viz., with the field and without the field. The computation by means of the above values gives

$$\eta_f/n_0 \approx 0.995$$

a quantity which can be observed. Worthing in his experiments found a value of 0.45 for this ratio<sup>2</sup> in disagreement with the result of our theory. It seems very probable that the surface conditions which have been neglected play

a very important rôle for the rate of evaporation at least. In regard to the increase of the heat of evaporation by an electric field the effect of these surface conditions may be different, perhaps negligible.

#### CONCLUSIONS

The vaporization of a solid is shown to be affected by a non-homogeneous electric field. Its influence consists in increasing the heat of vaporization by an amount which is too small to be measured experimentally. The second effect which is observable is a decrease in the rate of evaporation.

These conclusions, however, are subject to the following restrictions:

1. The density of the saturated vapor has been supposed so small that the interaction between the molecules or atoms can be neglected.

2. The evaporating substance is metallic, that is, the electric field does not penetrate into the body but stops abruptly on the surface.<sup>4</sup> In order to remove this restriction surface conditions would have to be considered, of which we know very little accurately; the "free" electrons inside the metal would also come into play. However, it may be that this assumption of discontinuity of the field and of uniform distribution of charges over the surface is responsible for the difference between the observed and approximately calculated values of the rate of evaporation. The experiments of Worthing might also be explained on this basis. These effects will be considered in a paper to be published later.

3. The value of  $\beta$  has been assumed so small (it always is according to the experimental data) that terms containing it as a factor have been neglected.

4. In view of the disagreement between theory and experiment this paper must be considered as preliminary.

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<sup>4</sup> J. Frenkel, *Zeits. f. Physik* **29**, 214 (1924); A. T. Waterman, *Proc. Royal Soc.* **A121**, 28 (1928).

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