On the Speed of Sublimation and Condensation

K. F. Herzfeld

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K. F. HERZFELD, *The Johns Hopkins University*

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It has been assumed that in the simplest case every atom that hits a crystal surface of the same material condenses. The corresponding speed of sublimation had been calculated theoretically. The formula for the equilibrium pressure is changed in the case of atoms, if the electron weight in the gaseous state is different from the solid state. The influence of this fact on the speed of sublimation is discussed in the first part of the paper and it is shown that for true metals the speed of sublimation is probably increased, while for non-metals a reflection coefficient exists. For molecules the equilibrium pressure is higher than for atoms because in sublimation there is a transition from a limited oscillation of the axes to free rotation. It is made plausible that this results in an increased speed of sublimation but a finite reflection coefficient might also occur.

STATISTICAL mechanics determines uniquely the vapor pressure or the equilibrium density of the saturated vapor over a crystal. On the other hand, equilibrium is present if the number of evaporating molecules is equal to that of the condensing. This relation is discussed in the following for several cases. It has a close connection with two recent papers that correlate the reaction velocity with the type of bond affected by the reaction.[1]

I. ATOMS

Given a crystal made up of atoms that have no resultant moment j; let Q_0 be the extrapolated heat of sublimation at zero temperature. Let furthermore ν be the (geometrical) average of the frequencies of vibration present in the crystal, then if the temperature is high enough to have classical specific heat $3R$, the number of vapor atoms per cc N_0 is given by[2]

$$N_0 = (2\pi M/RT)^{\frac{3}{2}}\nu^3 \exp(-Q_0/RT) = K_0. \quad (1)$$

If the temperature is so low that the specific heat of the solid is zero,

$$N_0 = (2\pi MRT)^{\frac{3}{2}}(Lh)^{-3} \exp(-Q_1/RT) = K_0' \quad (2)$$

(where L is the number of molecules per mole and Q_1 is Q_0 minus the zero point energy). In equilibrium the number of molecules condensing is[3]

$$(RT/2\pi M)^{\frac{1}{2}}N_0 \quad (3)$$

if one assumes that all atoms hitting the surface actually condense.[4] If we designate the number of atoms evaporating under this condition per second and cm² with k_0 and abbreviate

$$w = (RT/2\pi M)^{\frac{1}{2}}, \quad (3')$$

the x component of the average thermal velocity in the gas, there is in equilibrium:[5]

[1] O. K. Rice and H. Gershinowitz, J. Chem. Phys. 2, 853 (1934); H. Eyring, J. Chem. Phys. 3, 107 (1935).
[2] K. F. Herzfeld, *Kinetische Theorie der Wärme*, Braunschweig, 1925, p. 223.
[3] I. Langmuir, Phys. Rev. 8, 149 (1916).
[4] This is in agreement with experiments on Hg, Cd, Zn by M. Knudsen, Ann. d. Physik 50, 472 (1916); and R. W. Wood, Phil. Mag. 30, 300 (1915); 32, 364 (1916).
[5] The formula for k_0 which results from (4) has been deduced from kinetical considerations directly on p. 232 of book cited, footnote 2; see also R. Becker, Zeits. f. Physik 28, 256 (1924).

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$$k_0 = wN_0 \quad \text{or} \quad k_0 = wK_0, \tag{4}$$

or, at low temperatures

$$k_0' = wK_0'. \tag{4'}$$

Assume now we have an atom that has in the gaseous state a moment j, therefore an electron weight

$$g_v = 2j+1,$$

while the crystal is not distinctly paramagnetic (this includes metals) so that the electron weight in the crystal is 1.

Then we have to replace (1), (2) by

$$N = K_0 g_v \quad \text{or} \quad N = K_0' g_v. \tag{5}$$

If we call now the speed of evaporation k or k', we find

$$k = wN\alpha, \tag{6}$$

where $1 - \alpha$ is the reflection coefficient, i.e., the fraction of the atoms that hit the surface but do not stick. Defining now a number β, $k = k_0 \beta$, we find

$$\beta/\alpha = g_v. \tag{7}$$

The discussion is mainly concerned with (7).

(a) Emission of free electrons from a metal

Here $g_v = 2$. The direct calculations of Nordheim[6] show that $\alpha = 1$, $\beta = 2$. The physical reason for this is that an electron entering the metal has such a high energy that it gets into an empty part of the energy band of the metal and can therefore enter, independent of the direction of its spin. On the other hand, there are, because of the spin, twice as many electrons of a given state in the metal than without spin, and therefore $\beta = 2$.

(b) Metal with one valence electron in $S_{1/2}$

Here again $g_v = 2$, because of the two possible spin orientations, while the experimental fact that there is no strong, temperature dependent paramagnetism shows that we need not consider different orientations in the crystal. Two cases must now be distinguished.

(b')

If the solid is a true metal and can therefore be considered according to Wigner, Seitz and

[6] L. Nordheim, Zeits. f. Physik 46, 833 (1928); Proc. Roy. Soc. A121, 626 (1928).

Slater[7] as a lattice of positive ions surrounded by a sea of Fermi-electrons, one should expect $\alpha = 1$. Each condensing atom would create two new neighboring states of opposite spin and therefore the electron of the condensing atom, in dissociating off, would find a ready free level. The ion, of course, having $j = 0$, would always fit. This result is in agreement with Knudsen's experiments, who found that every atom of Ag and Cu condensed.[8] One must, however, account then for $\beta = 2$ as a consequence.

The electron of a condensing atom will in general get into the free part of the energy band and drop down later. Therefore, from the principle of detailed balancing, one would expect that an ion ready to evaporate would in general pick up one of the few electrons in the unfilled part of the band. There will be accordingly certain electron states of energy Q_0'/L in which the electron "belongs" to a certain ion. The fraction of the ions that will have electrons in these states will be

$$2e^{-Q_0'/RT}, \tag{8}$$

the factor 2 coming from the two possible spin directions. The number of ions having such electrons that evaporate per second is then given by the formula (4) in which $Q_0'' = Q_0 - Q_0'$ is inserted, multiplied with (8), which gives $\beta = 2$. If the one valence electron is in a state different from S in the vapor, while the conditions in the solid are as described here, the above considerations hold with

$$g_v = 2j+1, \quad \beta = 2j+1.$$

(b'')

If, on the other hand,[9] it were possible to condense these atoms into a monatomic, non-metallic, diamagnetic crystal, in which, therefore, the atoms keep their valence electrons and have orientations of the moment fixed in the lattice, g_v would still be 2 (or $2j+1$ in general), g_s, the weight in the solid, 1. But now the considerations that led to the deduction of the evaporation

[7] J. C. Slater, Rev. Mod. Phys. 6, 209 (1934).
[8] M. Knudsen, Ann. d. Physik 50, 472 (1916).
[9] A distinction analogous to that between (b') and (b'') is also made by J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford, 1932, p. 283, cases e, f.

formula (4) are valid without change, therefore $\beta = 1$ and α must be $\frac{1}{2}$ (or $1/(2j+1)$ in general). This can easily be understood. If an atom comes down from the gas, only half (or in general the fraction $1/(2j+1)$) of the places on the crystal on which it can alight have as permitted direction of moment the one which the incoming atom has; this results in a reflection coefficient of the magnitude given above. Formally one can compare (b') and (b'') so: A condensing atom with one valence electron creates two new states in the electron term-scheme of the crystal. But in the case (b') the two levels corresponding to the two spin directions are very close together, in the case (b'') rather far (i.e., much farther than kT) apart.

(b''')

If the crystal should be strongly paramagnetic, so that the j in both states would be the same and the components in the direction of a magnetic field the same, $g_v = g_s$, $\alpha = \beta = 1$.

II. MOLECULES

We assume that the molecule in the crystal has, besides the vibrations of its center, rotatory oscillations of its axes (or axis for a linear molecule) around an equilibrium position.[10] We assume the temperature to be so high that these oscillations have their classical specific heat ($3R$, or $2R$ for a linear molecule), and that the specific heat of rotation in the gas has the classical specific heat ($(3/2)R$, or R for a linear molecule). Finally we assume that there is either no difference between the internal vibrations of the molecule in the gas and in the solid (the ν's remaining unchanged) or that in both states they do not contribute to the specific heat.

The vapor pressure formula is then

$$N = K_0 K_r. \tag{9}$$

Here K_r is the ratio of the phase integrals of the rotational coordinates in the gaseous and the solid state. In classical calculations the phase integral can be split into a factor depending

[10] D. H. Andrews, Proc. Amst. Acad. **29**, 744 (1926); see also A. Eucken, Jahrb. f. Rad. **16**, 364 (1920); A. Eucken and E. Karwat, Zeits. f. physik. Chemie **112**, 479 (1924); A. Eucken and F. Fried, Zeits. f. Physik **32**, 151 (1925); F. Simon, ibid. **31**, 225 (1925).

only on kinetic energy and momenta and one depending only on potential energy and coordinates. The former is independent of the forces and therefore the same for the gas and the crystal. Accordingly it drops out of K_r, which can then be written

$$K_r = \Phi_g \cdot \Phi_s^{-1}, \tag{10}$$

where Φ is only the integral over the coordinate space.

But we have always

$$\Phi_g \gg \Phi_s.$$

These quantities are, namely, the average steric angles covered by the motion and these are always much smaller for the crystal than for the unhampered rotation of the gas.

For example, for a diatomic molecule with unequal atoms (symmetry number 1), Φ_g is simply the full spherical angle 4π, while

$$\Phi_s = \int d\varphi \int \exp\left(-IL\omega^2\vartheta^2/2RT\right) \sin\vartheta d\vartheta, \tag{11}$$

where I is the moment of inertia, ω the average frequency of oscillation. This gives (putting ϑ for $\sin\vartheta$)

$$\Phi_s = 2\pi RT/I\omega^2 L,$$

or, e.g., with $\omega = 3.10^{13}$, $I = 10^{-39}$, $T = 300$.

$$\Phi_s = 4\pi \cdot 0.02$$

or $K_r \sim 50$.

We have then in general

$$\beta/\alpha = \Phi_g \Phi_s^{-1} \tag{12}$$

and again the question arises:

is $\beta = \Phi_g \Phi_s^{-1}$, i.e., very great, and $\alpha = 1$ (13')

or $\beta = 1$, $\alpha = \Phi_s \Phi_g^{-1}$, i.e., very small   (13'')

or does something between these extremes happen? Experimental results seem not available.

We are going to show that (13') and (13'') follow clearly from two different assumptions. The assumption leading to (13') seems more probable.

The question is the following. The heat of sublimation per mole, extrapolated to $T = 0$, is Q_0. Consider a molecule in its heat motion. Assume that in a given moment it has a potential energy

(calculated from the equilibrium position) of ϵ, which is made of two parts, ϵ_t which is due to the deviations of the center of gravity of the molecule from its equilibrium position, and ϵ_r, which is due to a rotation of the axes out of the equilibrium orientation. If now the kinetic energy necessary to tear the molecule loose is given by

$$\epsilon' = Q_0/L - \epsilon = Q_0/L - \epsilon_t - \epsilon_r, \qquad (14')$$

that is, if the potential energy stored up by the oscillation of the axes is available for sublimation, (13') holds. If, on the other hand, it is not available, that is, if the energy necessary to sublimate this molecule is

$$\epsilon' = Q_0/L - \epsilon_t \qquad (14'')$$

(13'') is true.

To prove that, start with the latter, simpler case. Then the deduction given for $k = k_0$ can be taken over without change, $\beta = 1$. $\alpha = \Phi_s \Phi_g^{-1}$ can then be understood so that only such molecules can be condensed which come down under such an angle of the axes with the equilibrium position as it occurs at the temperature T in the crystal. (This is, of course, to be understood in the proper way, i.e., considering the distribution law.) The fraction of these properly oriented molecules is obviously given by the value of α mentioned above.

If, on the other hand, (14') is true, we have to modify the deduction leading to (4) in the following manner:

Call q in general the coordinates that characterize the orientation of the axes, dq the corresponding element in the phase space. Then the fraction of the molecules that have deviations from the position of equilibrium between x and $x+dx\cdots$ and a direction of the axes between q and $q+dq$ is

$$\nu^3 (2\pi M/RT)^{\frac{1}{2}} e^{-L\epsilon_t/RT} dx dy dz$$

$$\times \Phi_s^{-1} e^{-L\epsilon_r/RT} dq. \quad (15)$$

The number of molecules hitting the surface (y, z plane) so that $m\dot{x}^2/2 \geqq Q_0/L - \epsilon$ is

$$n'(M/2\pi RT)^{\frac{1}{2}} \int_{(Q_0-L\epsilon)}^{\infty} \dot{x} \exp(-M\dot{x}^2/2RT) d\dot{x}$$

$$= n'(RT/2\pi M)^{\frac{1}{2}} e^{-(Q_0-L\epsilon)/RT}, \quad (16)$$

where n' is the number of the particular molecules per cc. Inserting (15) into (16) and integrating over $dxdydz$ and dq, one finds as number of evaporating molecules

$$\nu^3 (2\pi M/RT)^{\frac{1}{2}} \exp -(Q_0/RT)(RT/2\pi M)^{\frac{1}{2}} \Phi_s^{-1} \int dq$$

$$= k_0 \Phi_s^{-1} \int dq. \quad (17)$$

But $\qquad\qquad \int dq = \Phi_g, \qquad\qquad (18)$

and therefore $\qquad \beta = \Phi_g \Phi_s^{-1}$.

In (18) it is understood, that the integration is to be taken according to classical physics, so that for example for a diatomic molecule with equal atoms, symmetry number 2,

$$\int dq = 2\pi = 4\pi/2.$$

In that case, $\alpha = 1$. To understand why under these assumptions even badly oriented molecules condense, one has to reverse the reasoning used for (15'). The large forces involved in the large heat of condensation Q_0/L are sufficient to force the molecule into the lattice in whatever orientation it arrives, providing the necessary potential energy ϵ_r.

Under both assumptions (14') and (14''), the kinetic energy of the oscillation of the axes is not involved in the process of sublimation. That means that each molecule keeps the angular momentum it had just before sublimation also in the gaseous state and each molecule keeps the angular momentum in the moment of condensation it had just before. Of course, angular momentum begins to change immediately after condensation, because of the forces now acting on the molecular orientation.

If the temperature rises so high that the molecules rotate almost freely in the crystal,

$$\Phi_g \sim \Phi_s, \quad \beta = \alpha = 1.$$

III. REFINEMENT OF THE THEORY

In the preceding deductions, one assumption has been made that might be wrong. The reasoning leading to (4) said: The number of atoms that have a deviation from the equilibrium position between x and $x+dx\cdots$ and evaporate per second is

$$n'(RT/2\pi M)^{\frac{1}{2}} \exp(-Q_0 + L\epsilon_t/RT), \quad (19)$$

where ϵ_t is the potential energy connected with that deviation and n' the number of atoms per cc having this deviation. One then inserted n' from the Maxwell-Boltzmann distribution law and integrated over $dxdydz$. But that is correct only if in the permitted range $L\epsilon_t < Q_0$. Otherwise, one can only integrate to such values of x, y, z in (19) that

$$L\epsilon_t = Q_0.$$

Call $\qquad \int_0^{L\epsilon_t=Q_0} dxdydz = 1/n''.$

Then, in the simplest case, the number of evaporating atoms is

$$nk_0/n'' = \alpha' k_0,$$

where n is, as before, the number of atoms per cc, and speed of sublimation and speed of condensation have both to be multiplied by $\alpha' < 1$ in all the cases treated in I. The same is true for molecules and assumption (14''). Possibly Volmer's[11] experiments showing a reflection coefficient of Hg on mercury crystals of 10 percent can be explained so.

[11] M. Volmer and I. Estermann, Zeits. f. Physik **7**, 1 (1921).

Similarly for molecules, we have to change the discussion of assumption (14') so that we integrate only to such values of the coordinates in the crystal that satisfy

$$Q_0 > L(\epsilon_t + \epsilon_r).$$

The speed of sublimation $k_0\beta$ has again to be multiplied by a factor α' smaller than 1,

$$\alpha' = n\Phi_g^{-1} \int_0^{L\epsilon=Q_0} dxdydzdq = \Phi'\Phi_g^{-1}$$

and the same factor enters the formula for the speed of condensation, giving rise to a reflection coefficient of $1 - \alpha'$.

The physical reason for the existence of this reflection coefficient is, of course, that the attractive forces that are responsible for the heat of sublimation can force the incoming molecule only into the fraction α' of the total coordinate space.

We have then an intermediate case between (13') and (13'') where

$$k = k_0\beta', \quad \beta' = \Phi'\Phi_s^{-1}, \quad \alpha' = \Phi'\Phi_g^{-1}.$$

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Non-Silicates with Cristobalite-Like Structure

Tom. F. W. Barth, *Geophysical Laboratory, Carnegie Institution of Washington*
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The cristobalite type of structure which has been previously observed in certain silicates: carnegieite, $NaAlSiO_4$, and Na_2CaSiO_4 is now shown to occur in $K_2O.Al_2O_3$, $K_2O.Fe_2O_3$, and $Na_2O.Al_2O_3$.

A NEW cubic compound, $K_2O.Al_2O_3$, has recently been described by Brownmiller,[1] and measurements on an x-ray powder photograph of it have been published.[2] This powder

[1] L. T. Brownmiller, *A Study of the System Lime-Potash-Alumina*, Am. J. Sci. **29**, 260 (1935).

[2] The reflections observed by Brownmiller correspond to cubic symmetry (length of the edge of the unit cube, $a = 7.69A$), except for three weak lines, corresponding to a planar spacing of 2.395, 2.000 and 1.488. He states, however, that $K_2O.Al_2O_3$ is extremely hygroscopic so there were considerable difficulties in taking the photograph; it is probable, therefore, that these weak reflections come from some alteration product on the surface of the crystals.

photograph is very similar to that of $K_2O.Fe_2O_3$, and they both resemble the x-ray patterns of certain silicates structurally isomorphous with cristobalite (see Table I). These similarities indicate that the structure of $K_2O.Al_2O_3$ and of $K_2O.Fe_2O_3$ may in some way or other be related to that of cristobalite.

The well-known feature of the cristobalite structure is the existence of endless silicon-oxygen chains with large, open spaces in between. It seemed probable, therefore, that in $K_2O.Al_2O_3$ there would be corresponding chains of alumi-