CONNECTION BETWEEN THE PARAMETERS OF AN EVAPORATING MATERIAL AND THE GASEOUS MEDIUM SURROUNDING IT

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Equations connecting the temperature of an evaporating material with the parameters of the surrounding medium are established and the results of an experimental verification of these equations are presented. The possibility of applying the results obtained to the exact determination of diffusion coefficients is illustrated.

We will consider the case of evaporation (sublimination) of a spherical particle in the absence of the complicating effect of free convection (a rarefied medium with $Gr < 1$, although in this case $Kn \ll 1$) and under conditions where the radiative heat exchange is small compared with conductive heat exchange. The experimental verification and numerical estimates are given for the case of the sublimation of ice. The solution of this problem, in addition to direct technical application such as for the calculation of the process of sublimative dehydration in a medium of noncondensing gases or the determination of the partial pressure of vapors from the temperature of an evaporating body, can be used for the calculation of diffusion coefficients, as is shown below.

The problem is solved in a quasi-stationary approximation under the conditions of negligibly small total pressure gradients, constant λ, and variable D which depends on the temperature according to the law

$$D = D^0 (T/T^0)^n, \tag{1}$$

where n = 0, 3/2, and 2.

The system of differential equations describing the process has the form

$$\frac{d}{dr}(r^2\rho v) = 0, \tag{2}$$

$$\frac{d}{dr}\left(r^2\lambda\frac{dT}{dr}\right) - \rho v c_p \frac{dT}{dr} = 0, \tag{3}$$

$$\frac{d}{dr}(r^2\rho v c) + \frac{d}{dr}(r^2 j) = 0. \tag{4}$$

Boundary conditions: for $r = r_0$

$$\lambda\frac{dT}{dr} = \mu H, \tag{5}$$

$$\rho v = \mu, \tag{6}$$

$$\rho v c + j = \mu, \tag{7}$$

for $r = r_1$

$$T = T_1, \tag{8}$$

$$p = p_1. \tag{9}$$

The joint solution of Eq. (2) with the boundary conditions (6) and Eq. (3) with the conditions (5) and (8) makes it possible to find an expression for the sublimation rate

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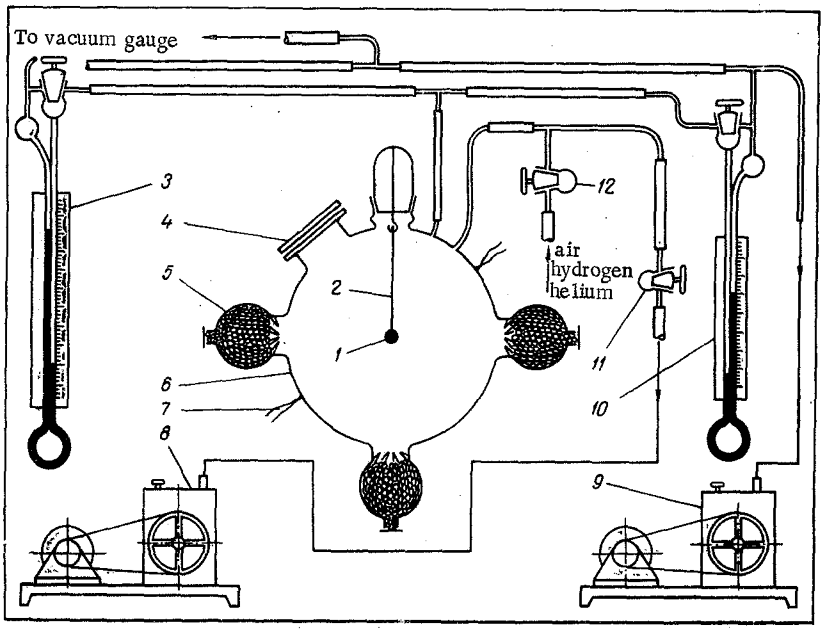

Fig. 1. Diagram of experimental apparatus: 1) specimen; 2) glass fiber; 3) dibutylphthalate manometer; 4) observation window; 5) flasks containing zeolite; 6) experimental chamber; 7) thermocouple; 8, 9) vacuum pumps; 10) mercury manometer; 11) vacuum valve; 12) leak valve.

$$\mu = \frac{\lambda}{c_p}\,\frac{r_1}{r_0(r_1-r_0)}\ln\left(1+\frac{T_1-T_0}{H}c_p\right). \tag{10}$$

To determine the unknown T_0 which enters into (10) we use (4) and the conditions (8) and (9), first making a substitution of variables in (4) according to the equation

$$c = \left[1-\frac{M_2}{M_1}\left(\frac{P-p}{p}\right)\right]^{-1}. \tag{11}$$

We obtain

$$\frac{\lambda}{c_p}\ln\left(1+\frac{T_1-T_0}{H}c_p\right) = \frac{P^0D^0}{T_{ef}R_1}\ln\left(\frac{P-p_1}{P-p_0}\right). \tag{12}$$

Here when n = 0

$$T_{ef} = T_0-\frac{H}{c_p}+\frac{T_1-T_0}{\ln\left(1+\frac{T_1-T_0}{H}c_p\right)}, \tag{13}$$

when n = 2

$$T_{ef} = \frac{c_p(T^0)^2}{H-c_pT_0}\left[\frac{\ln T_1-\ln T_0}{\ln\left(1+\frac{T_1-T_0}{H}c_p\right)}-1\right], \tag{14}$$

and when n = 3/2

$$T_{ef} = \frac{2(\sqrt{T^0})^3}{\sqrt{\frac{H}{c_p}-T_0}\,\ln\left(1+\frac{T_1-T_0}{H}c_p\right)} \times \mathrm{arctg}\left[\frac{(\sqrt{T_1}-\sqrt{T_0})\sqrt{\frac{H}{c_p}-T_0}}{\frac{H}{c_p}-T_0+\sqrt{T_1T_0}}\right]. \tag{15}$$

TABLE 1. Experimental and Theoretical Values of P (mm Hg) for Sublimation of Ice in Air

Temperature, °K	Experimental data	Calculation according to (12) with T_{ef} from:		
		(14)	(15)	(13)
293	535,8	555,1 ± 7,7	545 ± 14,0	516 ± 4,5
299	410,7	432 ± 7,7	422 ± 14,0	394 ± 4,5
303	361,6	377 ± 7,7	368 ± 14,0	339 ± 4,5

In the solutions presented, unlike the well known solutions of [1, 2] which pertain to analogous cases, allowance is made for the variation in temperature along the direction of diffusion.

Actually, if both sides of Eq. (12) are multiplied by the complex $r_1/r_0(r_1-r_0)$ then its right side will represent an expression for the mass flow in the form characteristic of the Stefan equation, which the effect of the variability of D is manifested through the expression for Tef.

It must be noted that even with a constant D(n = 0) the adoption for T_{ef} of the arithmetic mean value is correct only with the accuracy provided by retaining two terms of the Taylor series expansion of the logarithm entering into the expression for T_{ef}.

To test the results of the theory and to determine the most suitable expression and dependence on the temperature for D we conducted an experimental study.

An experimental test of the results of the theory could be accomplished in principle either by measuring the sublimation rate or by comparing the values of the parameters measured in the experiment with those obtained from the corresponding solutions.

Both methods in one or another form have been used earlier by investigators [3-6] to study the evaporation of drops. In this case, however, complications arose caused by heat fluxes unavoidably resulting from the use of thermocouples. The reduction in the relative fraction of these heat fluxes by increasing the size of the specimen is limited by the increase in the radiative heat flux.

These difficulties could be avoided by some changes in the experimental method. In contrast to the well-known works [3-6], in our experiments we determined the pressure corresponding to a strictly determined temperature of the specimen, its melting temperature. The moment of melting was determined visually without difficulty. It is important to emphasize the necessity of determining just the temperature of the start of melting and not of freezing, since otherwise an error is possible because of supercooling of the specimen.

A diagram of the apparatus is presented in Fig. 1. The spherical specimen 1 with a diameter of 2-3 mm was suspended on a glass fiber 2 with a diameter of 0.004-0.005 mm. The chamber was thermostatically regulated and after preliminary evacuation and purging it was filled with the required gas. The value 11 was closed and the chamber was gradually filled through the leak valve 12. At the moment the ice started to melt the pressure in the chamber was determined using the U-shaped manometers 3 and 10, filled with dibutylphthalate and mercury, respectively. Both manometers were connected with a low-pressure line in which the vacuum was maintained by the pump 9 and monitored with a type VT-3 thermocouple vacuum gauge. Zeolite, which was placed in the 10 flasks 5 (only three are shown in Fig. 1) uniformly distributed over the surface of the chamber, was used to absorb the vapors released in the sublimation process. The window 4 was provided for visual observation of the state of the specimen.

The experimental verification was conducted in a medium of air, since in this case we have more reliable data available for the coefficient λ and D^0.

The experimental results are presented in Table 1.

As seen from Table 1, the experimental data are closest to the theoretical data calculated from Eq. (12) with the Tef corresponding to n = 3/2 in (1).

It should be pointed out that the experimental determination of the pressure was made for a precisely determined specimen temperature. Actually, the derivatives (for the parameters of the present experiment) are: $\partial P/\partial T_0 = 51.4$ mm Hg/deg; $\partial P/\partial T_1 = -18.01$ mm Hg/deg; $\partial P/\partial D^0 = 4.33 \cdot 10^4$ mm/m²/h; $\partial P/\partial \lambda = -2.2 \cdot 10^4$ mm Hg/kcal/m · h · deg.

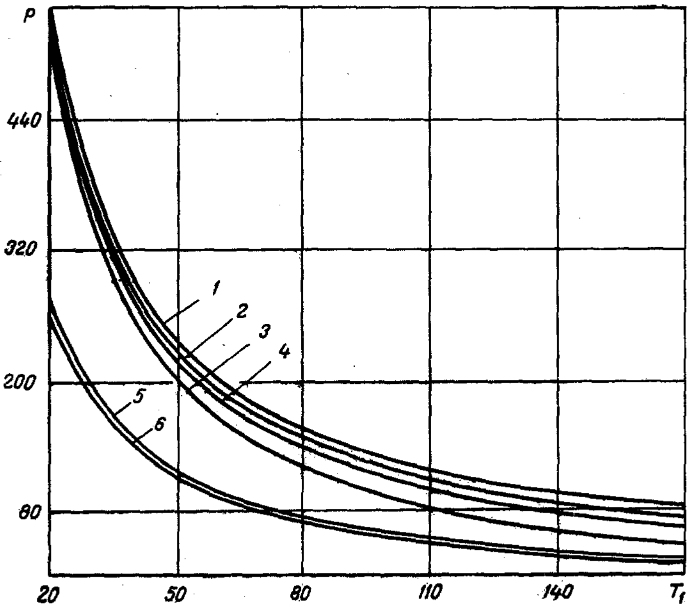

Fig. 2. Limiting values of pressure P (mm Hg) as a function of the temperature T_1(°C): 1) for the sublimation of ice in air, calculated from Eq. (12) with T_{ef} corresponding to (14); 2) to (15); 3) to (13); 4) calculated from Eq. (16); 5) for sublimation of ice in helium, calculated from Eq. (12) with T_{ef} from (15); 6) same in hydrogen.

If it is considered that the accuracy in measuring the pressure is not less than 0.1 mm Hg in any case, to achieve such an experimental accuracy in the measurement of T_0 (as is usually done) would require that this temperature be measured with an accuracy of 0.002°C.

Because of the high accuracy of this method it can be used to determine the coefficients D^0. We determined these coefficients for two important cases: in the systems of water vapor—hydrogen, and water vapor—helium.

The coefficient of diffusion of water vapor in hydrogen was 0.975 ± 0.002 cm^2/sec (P^0 = 760 mm Hg, T^0 = 34°C), while for helium it was 0.908 ± 0.002 cm^2/sec (same conditions).

The values of D^0 in the water vapor—helium system are in good agreement with the experimental data of other authors [7, 8].

For the water vapor—hydrogen system the coefficient of diffusion occupies an intermediate value among the experimental results known from the literature [7, 9, 10], and corresponds almost exactly to the theoretical value calculated from the well known equations of the molecular theory of gases when the Lennard—Jones potential is used to describe the intermolecular interaction [11].

Since the direct application of Eq. (12) presents certain difficulties it is important to have simplified equations to estimate the connections between the parameters. As the first simplification one can examine this dependence with T_{ef} calculated from (13) (the coefficient of diffusion does not depend on the temperature). If in this expression one in turn replaces the logarithm entering into T_{ef} with the first two terms of the Taylor seriesexpansion, andin the expansions of the other two logarithms one keeps only the first term, oneobtains the simple equation

$$\lambda \frac{T_1 - T_0}{H} = \frac{2P^0D^0}{R_1(T_1 + T_0)} \frac{p_0 - p_1}{P}. \tag{16}$$

In using Eqs. (12) and (15) one must keep in mind the relationship [12]

$$\ln p_0 = A - \frac{B}{T_0}, \tag{17}$$

where A = 24.38 and B = 6236.

The results of a calculation on an electronic computer carried out according to Eqs. (16) and (12) with the different T_{ef} of (13)-(15) are presented in Fig. 2.

As is seen, Eq. (16) is quite applicable for estimating calculations. The results of an analogous calculation for the sublimation of ice in a medium of hydrogen and of helium are also presented here. Their analysis shows that the limiting pressures which ensure that the process will proceed are considerably lower in media of hydrogen or helium than in air for the same temperature.

The choice of the temperature $T_0 = 0°C$ was stipulated by the fact that it determines the value above which the sublimation process is impossible.

Using the equations obtained one can determine the pressure in an apparatus or select the appropriate mixture of gases and its temperature for the attainment of a desired effect in organizing the process of sublimative dehydration.

NOTATION

D	is the coefficient of diffusion;
λ	is the coefficient of thermal conductivity;
ρ	is the density of mixture;
v	is the linear velocity;
r	is the coordinate;
$c = \rho_1/\rho$	is the mass concentration;
ρ_1	is the partial density of vapor;
$j = -D\rho(dc/dr)$	is the diffusional flux;
T	is the temperature;
P	is the partial pressure;
$\mu = -\rho_T(dr/d\tau)$	is the rate of sublimation;
ρ_T	is the density of subliming material;
M_1, M_2	are the molecular weights of vapor and gas, respectively;
τ	is the time;
c_p	is the heat capacity of vapor;
H	is the heat of phase transition;
$R_1 = R/M_1$	is the individual gas constant for water vapor;
D^0	is the coefficient of diffusion determined at some temperature T^0 and pressure P^0.

Subscripts

0 and 1 are the indices pertaining to the values of the variables at the surface of the phase transition and at some distance from it.

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