

PECULIARITIES OF WATER DROPLET EVAPORATION AT A CONSTANT TEMPERATURE

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We have analyzed the experimental data on evaporation of water droplets in a wide range of pressure (760–15 mm Hg) at a constant temperature. It is shown that, at pressure lower than 100 mm Hg (in the so-called transient regime of evaporation), formulas of the conventional theory depart from the experimental data. These departures increase with decreasing in pressure. We have found that, in the transient evaporation regime, the condensation coefficient of water α of a water droplet depends on its radius r according to the phenomenological relation $r \cdot \alpha = \text{const}$. We have proposed a formula for the water droplet evaporation rate at a constant temperature that describes the experimental data in the entire range of pressure, even at low pressures where the conventional theory does not correspond to the experimental data.

Introduction

The consistent theoretical description of evaporation of liquid and solid droplets that starts from the first principles requires solving the problem of physical kinetics with the formulation of adequate boundary conditions on the droplet surface. Unfortunately, a realization of this approach at the moment is connected with serious mathematical complexities. Moreover, the final analytic expressions obtained within the framework of some simple models are, as a rule, too cumbersome and cannot be reliably compared with experiment.

Bhatnagar, Gross, and Krook (BGK) proposed the simplified procedure of solving the kinetic Boltzmann equation. Numerical solutions of the Boltzmann equations with the collision term in the BGK form were found in [2]. At the same time, the distribution function contained some numerical parameter that was chosen from a condition of the best fitting with the experimental data. The physical meaning of this parameter is the condensation coefficient. We will discuss this coefficient below in detail by using a phenomenological approach.

To our mind, the last approach is more efficient from the implementation point of view. At the relatively high evaporation rates or in the transient regime of evaporation, the main problem is a fitting of two

regimes. The first one is the kinetic regime that corresponds to the free evaporation of a liquid from the droplet surface within a domain of a few mean free paths in size. The second regime corresponds to the subsequent diffusion withdraw of the vapor through a buffer gas (diffusion regime). This approach is based on the phenomenological Fick law that allows one to obtain the Maxwell formula of the evaporation rate of spherical droplets. It is in a good agreement with experiment for very small Knudsen's numbers $\text{Kn} = \lambda/r \ll 1$ (λ is the mean free path of molecules of a droplet of radius r) or under conditions of the diffusion evaporation. With increase in the Knudsen number or in the transient regime, one has to take into account the first-order corrections in the small parameter $\text{Kn} \ll 1$. They are responsible for jumps of the macroscopic quantities near the interface: temperature, concentration, and hydrodynamic velocity (for moving droplets) [3].

The Maxwell formula admits the introduction of different corrections depending on the evaporation regime. In particular, the Fuchs correction to the Maxwell formula allows one to take into account a jump of concentration near the droplet surface. Fuchs and Sutugin have intensively developed this direction of the phenomenological theory [4–5].

In this paper, we have analyzed the experimental data on the water droplet evaporation in a wide range of pressure at a constant temperature that have been obtained in the Aerosol Laboratory of Kyiv University. Our main objectives are the study of the transient evaporation regime at a constant temperature and establishing the phenomenological relations between parameters that control the process.

1. Basic Formulas of Evaporation Theory

At very small Knudsen's numbers Kn at relatively high pressures (of the order of the atmospheric one), the evaporation rate of a droplet or the rate of decrease in the droplet surface $\dot{S}(t)$ is described by the well-known

Maxwell formula [4]

$$\frac{dS}{dt} \equiv \dot{S} = \frac{8\pi D(C_0 - C_\infty)}{\rho}, \quad (1)$$

where D is the diffusion coefficient of vapor molecules in a buffer gas, C_0 is the vapor concentration on the droplet surface, C_∞ is the vapor concentration at the infinite distance from the droplet, ρ is the droplet density.

The concentration of vapor on the droplet surface C_0 is usually accepted to be equal to a pressure of the saturated vapor $C_s(T)$ (T is a temperature of the droplet surface). This quantity as a function of the temperature and could be found in the tables for many liquids. It is clear that, in the regime of intensive evaporation, the concentration of vapor on the droplet surface differs considerably from the equilibrium concentration. Below, we show this by the direct experiments.

According to (1), the rate of varying the droplet surface (evaporation rate $\dot{S}(t)$) at fixed temperature and pressure is a constant. Therefore, $S(t)$ is a linear function of time. At the same time, the dependences of the droplet mass $m(t)$ and radius $r(t)$ are nonlinear functions of time. Further, we will study $\dot{S}(t)$.

It follows from (1) that $\dot{S}(t)$ is a linear function of inverse pressure $1/p$ at a constant temperature, as dictated by a dependence of the diffusion coefficient on p . The experiments confirm this only at comparatively high pressures. With a further decrease in the pressure, the experimentally measured evaporation rate grows but slower than the Maxwell formula requires. A disagreement between theory and experiment increases with $1/p$.

In fact, with decrease the pressure, one has to take into account the concentration jump. Formula (1) holds true provided that a withdraw of vapor from the surface is realized through the diffusion mechanism (in the diffusion approximation, the mean free path $\lambda \rightarrow 0$). The kinetic regime of evaporation takes place at low pressures at distances of a few mean free paths from the droplet surface Δ . In this domain, the vapor molecules pass the distance Δ with no collisions. Collisions and, as a consequence, the diffusion withdraw of vapor starts from the distance Δ where the vapor concentration is usually denoted by C_1 . From the continuity of the kinetic and diffusion fluxes of vapor, we could obtain the Maxwell formula with the Fuchs correction [4]

$$\dot{S} = -\frac{8\pi D(C_0 - C_\infty)}{\rho\left(\frac{D}{ru\alpha} + \frac{r}{r+\Delta}\right)}, \quad (2)$$

where r is the radius of a droplet, $u = v_T/4 = \sqrt{\frac{kT}{2\pi M}}$ is the fourth part of the mean average velocity of a molecule v_T (k is the Boltzmann constant, M is the mass of a molecule), α is the condensation coefficient. It is defined as a ratio of the number of molecules that condense on the surface to the total number of molecules that collide with the surface per unit time. This quantity could not be computed reliably at present time and is introduced in (2) as a phenomenological parameter. Another parameter Δ could be neglected provided that $\Delta \ll r$.

Now we consider the denominator of (2) to clarify its dependence on the Knudsen number $\text{Kn} = \lambda/r$. An evaluation of the diffusion coefficient $D = \frac{1}{3}v_T\lambda$ allows us to rewrite the denominator in the following way

$$\frac{D}{ru\alpha} + \frac{r}{r+\Delta} = \frac{4}{3\alpha}\text{Kn} + \frac{1}{1+\gamma\text{Kn}}, \quad \Delta = \gamma\lambda. \quad (2a)$$

Here, γ is a numerical coefficient.

For small $\text{Kn} \ll 1$, denominator (2) or expression (2a) to within linear terms in the small parameter may be presented as $1 + (\frac{4}{3\alpha} - \gamma)\text{Kn}$. Putting on an additional constraint $\alpha\gamma \ll 1$, we obtain the Maxwell formula with the Fuchs correction

$$\dot{S} = -\frac{8\pi D(C_0 - C_\infty)}{\rho\left(1 + \frac{D}{ru\alpha}\right)}, \quad \text{Kn} \ll 1, \quad \alpha\gamma \ll 1. \quad (3)$$

If the last inequality (3) is violated, one has to take into account corrections associated with Δ .

It is worth noting that different corrections may be introduced in the Maxwell formula. For example, in processing the experimental results, we used formula (3) with a correction on the Stefan flux [4]:

$$\dot{S} = -\frac{8\pi D(C_0 - C_\infty)}{\rho\left(1 + \frac{D}{ru\alpha}\right)} \cdot \text{St}, \quad \text{St} = \left(1 + \frac{p_0 + p_\infty}{2p}\right), \quad (4)$$

where p_0 is the pressure of the vapor on the droplet surface, p_∞ is the pressure of vapor far from the droplet, p is the pressure in the chamber, where evaporation is studied. The Stefan correction is considerable at low pressures.

As was mentioned above, there is no reliable theory of the condensation coefficient at the moment. A review of the experimental results on this issue is given in [6]. In this paper, we considered α as a fitting parameter and found it from the best agreement of the experimental curves $\dot{S}(1/p)$ with theoretical ones (3) or (4).

With a further decrease in the pressure, one could see that the experimental evaporation rate differs

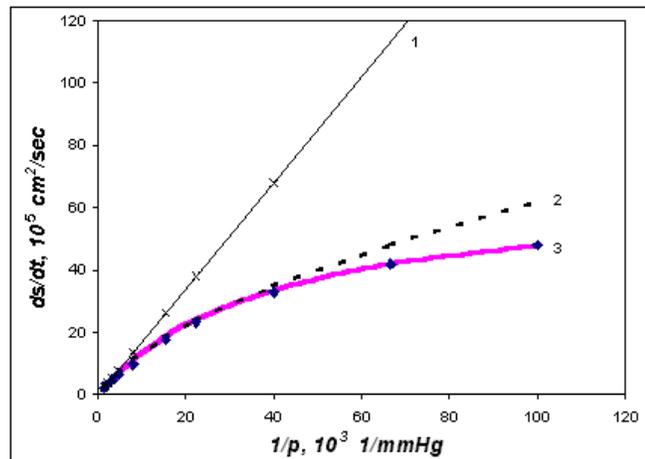


Fig.1. Evaporation rate of water droplets in neon atmosphere versus inverse pressure at a temperature of 10°C and a humidity of 75%. Experimental points — \blacklozenge ; calculations according to: Maxwell formula (1) — 1; Maxwell formula with Fuchs correction (2) — 2; phenomenological formula (8) — 3

from (4). Attempts to fit the theory and the experiment by choosing the proper fitting parameter with the help of (4) require relatively small α . In this case, $D/ru\alpha$ becomes of the order of unit and cannot be treated as a correction any more. Moreover, the small α that fit the experimental and theoretical dependences of the evaporation rates (4) at large $1/p$ spoil it at middle and small $1/p$.

To illustrate the peculiarities of droplet evaporation in a wide range of pressures, we present a typical experimental dependence $\dot{S}(1/p)$ in Fig.1 for water droplets and the same dependences according to the theoretical formulas (1) and (4). Based on the analysis of numerous experimental data on evaporation of droplets of different liquids, we could state that the entire range of pressures (from the normal up to very low ones) could be divided into four domains. Particularly, for water, we get:

1. High pressures (760–400) mm Hg, where the evaporation rate of droplets is described by the Maxwell formula (1).

2. Intermediate pressures (400–100) mm Hg, where the evaporation rate of droplets is described by formula (4) with the relevant condensation coefficient.

3. Low pressures (100–20) mm Hg, where the evaporation rate could not be described satisfactorily by formulas (1)–(4);

4. Evaporation in vacuum (free evaporation).

The first and fourth regimes have been much studied theoretically with sound experimental confirmation.

Below we consider the evaporation of water droplets in the regimes that correspond to the pressure ranges 2 and 3.

2. Evaporation of Water Droplets at a Constant Temperature

The experimental studies of evaporation of droplets of different liquids in a wide range of pressures in the atmosphere of different gases have been performed in the Aerosol Laboratory of Kyiv National University. The aim of these experiments was to establish the limits of applicability of formulas (1)–(4) and to compare the evaporation rates of liquid droplets under different conditions: under electromagnetic irradiation and in the dark regime (with no radiation) [7], in the presence of organic impurities in the atmosphere of different buffer gases and with no impurities [8].

It is necessary to note that the process of intensive evaporation of droplets is accompanied by a considerable cooling of the droplet surface. For example, under the evaporation of water droplets in the atmosphere of dry nitrogen when the pressure decreases from 750 to 15 mm Hg, their temperature drops from 12 to -5°C . An analysis of experimental results is considerably complicated by simultaneous formation of jumps in the temperature and concentration [9].

In due time, at the Aerosol Laboratory of Kyiv University, a special method that provides a constant temperature of evaporating droplets was elaborated [10]. Varying the pressure in a chamber was provided with the help of a special vacuum pump. The pressure in the chamber was measured by a mercury manometer and controlled by an electronic device. The hermetically closed chamber allowed one to conduct measurements at a constant pressure during a long time. A given humidity of the gas phase was kept by the saturated salt solutions.

The droplets were suspended on one junction of a thermocouple. The second junction was located pretty far from a droplet. The latter is heated by electric lamps whose radiation was focused on the droplet. An automatic device regulated an electric current in the lamps to provide the zero difference of temperatures between the droplet and the environment, $\Delta T = 0$.

To define the evaporation rate of a droplet, it was photographed in equal intervals of time along with a scale ruler. The photographs were processed by the method of graphic integration to define the droplet surface at every moment of time and the rate of its decrease \dot{S} . The error of the experiment was about 1–2%.

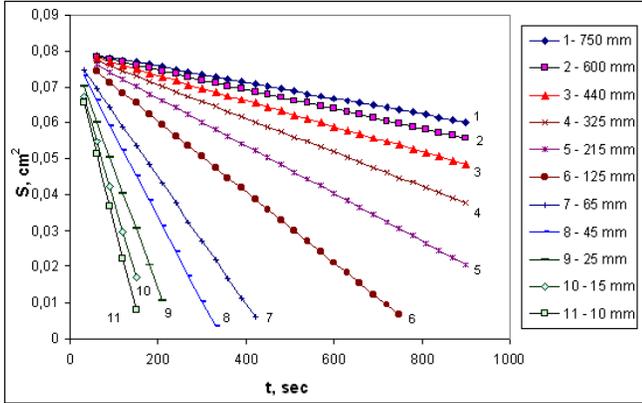


Fig.2. Experimental dependences of the droplet surface versus time $S(t)$ for evaporation in neon atmosphere at a temperature of 10 °C and a humidity of 75%, $p = \text{const}$ (mm Hg)

3. Dependence of the Condensation Coefficient on Droplet Radius

Figure 2 presents the experimental dependences of the water droplet surface on time $S = f(t)$ during evaporation in the neon atmosphere at a temperature of 20 °C for eleven different values of the pressure. It could be seen from Fig.2 that the dependences $S = f(t)$ are linear functions in the entire range of pressures. We obtained linear dependences for the evaporation of water droplets in the atmosphere of other gases as well. Further, we defined the evaporation rate for each value of the pressure from the slope tangent of lines $S = f(t)$ to the time axis.

The experimental dependences of the water droplet evaporation rates versus the inverse pressure $1/p$ in the definite range of pressure in the atmosphere of three gases (He, Ne, Ar) at a temperature of 10 °C and a humidity of 75% are presented in Fig.3. One could see that the evaporation rate is not a linear function of $1/p$ and considerably depends on the buffer gas.

The experimental dependences $\dot{S} = f(1/p)$ (Fig.3) were approximated by formula (4). The condensation coefficient α has been chosen from the best fitting of

Computed values of α for water droplets of different radii r and their product $r\alpha$ in the atmosphere He, Ne, Ar at 10 °C; humidity was 53% or 75%

Droplet radius, r , cm	Humidity 53%				Humidity 75%			
	Condensation coef. α			$r\alpha$, 10^4 cm	Condensation coef. α			$r\alpha$, 10^4 cm
	Ar	Ne	He		Ar	Ne	He	
0.03	0.016	0.016	0.016	4.8	0.014	0.014	0.014	4.2
0.056	0.009	0.009	0.009	5.04	0.0075	0.0075	0.0075	4.2
0.08	0.006	0.006	0.006	4.8	0.005	0.005	0.005	4.0

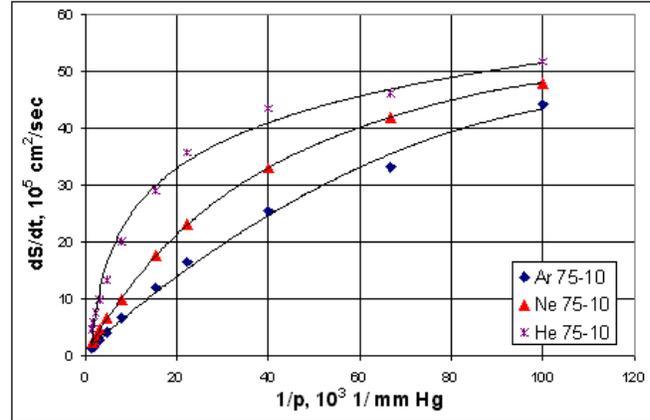


Fig.3. Experimental evaporation rate of water droplets versus inverse pressure in atmosphere of Ar, Ne, He at a temperature of 10 °C and humidity of 75%

experimental data. The values of α obtained while processing the experimental data are presented in the table.

From the table, one could see that the water condensation coefficient α at a constant temperature does not depend on a buffer gas provided that other conditions of evaporation are the same. It depends on the droplet radius r only. If we assume that α is a constant at a constant temperature (as it is meant in many papers), then the evaporation rate must change with varying the droplet radius. But it contradicts our experimental data (Fig.2). Therefore, we have to make an important conclusion that the product of the droplet radius r by the condensation coefficient α is a constant at a constant temperature:

$$r\alpha = \text{const} \cong 4.5 \cdot 10^{-4} \text{ cm.} \tag{5}$$

It is clear that this relation cannot be applied to the plane surface. Empiric relation (5) holds true in the transient regime of evaporation and gives an additional information on the condensation coefficient. It allows one to understand the dispersion in magnitudes of the condensation coefficient obtained by different authors experimentally. Unfortunately, in most papers, their authors did not indicate a size of the evaporating surface. Due to importance of this relation, we have checked it using one more approach (see the next section).

4. Dependence of the Vapor Concentration on the Evaporation Rate near a Droplet

In the process of intensive evaporation, the vapor concentration on the droplet surface C_0 departs from

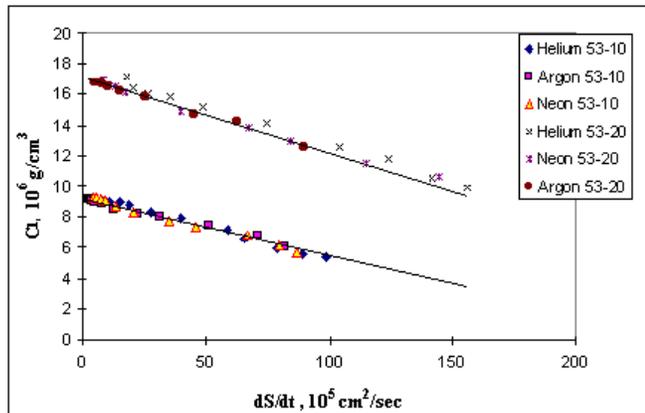


Fig.4. Concentration C_1 versus evaporation rate of water droplets in different gases at temperatures of 10 and 20 °C and a humidity of 53%

its equilibrium value and shows a dependence on the evaporation rate, in particular, on \dot{S} . To illustrate this, we have measured the evaporation rates of water droplets at a constant temperature in the atmosphere of different gases. Figure 4 presents the dependences of the vapor concentrations C_1 near the droplet surface on the evaporation rate \dot{S} calculated on the base of the experimental data with the help of (4)

$$\dot{S} = 8\pi D(C_1 - C_\infty)St/\rho \tag{6}$$

for two different temperatures, 10 and 20 °C. Here C_1 is the vapor concentration at a distance $r + \Delta$, where the diffusion mechanism of evaporation takes place. The dependences $C_1 = C_1(\dot{S})$ obtained with the help of (6) with regard for the experimental values of \dot{S} turned out to be linear functions and to within the experimental error coincided for all buffer gases at the same temperature. Only at very small \dot{S} , the concentration C_1 practically coincides with the concentration of equilibrium saturated vapor $C_0(T)$ at a temperature of the droplet surface (see Fig.4).

From the phenomenological point of view, the concentration C_1 for particular conditions of the experiment must be a function of the temperature and the evaporation rate $C_1 = C_1(T, \dot{S})$. At small \dot{S} , it may be presented as

$$C_1 \cong C_0(T) - \beta(T) \cdot \dot{S}, \tag{7}$$

where $\beta(T)$ is some coefficient that depends for a particular droplet-buffer gas system only on temperature T . According to our experimental data, $\beta(T)$ does not depend on a type of the buffer gas (Fig.4).

After the substitution of (7) into the Maxwell formula (1), we obtain a new formula for the evaporation rate of water droplets at a constant temperature

$$\dot{S} = \frac{8\pi D(C_0 - C_\infty)}{\rho(1 + 8\pi D\beta/\rho)}. \tag{8}$$

The coefficient β is a phenomenological parameter that equals the tangent of the slope of the straight lines (7) to the \dot{S} axis (Fig.4). Our experimental data give $\beta \cong 0.04 \text{ g} \cdot \text{s}/\text{cm}^5$. A structure of formula (8) is the same as the Maxwell formula with the Fuchs correction (4). But it is surprising that (8) describes the experimental evaporation rate of water droplets at a constant temperature in the entire range of pressures. One could see it from Fig.1 where curve (3) calculated with the help of (8) is in a very good agreement with the experiment.

To our mind, the existence of the connection between the droplet radius and the concentration coefficient is extremely important from the practical point of view. We decided to check (5) by using the following argumentation. A rate of varying the droplet mass $m(t)$ with time in the kinetic regime is given by the relation $\dot{m} = 4\pi r^2 \alpha u(C_0 - C_1)$. On the other hand, $\dot{m} = 4\pi r^2 \dot{r} \rho$ and $\dot{S} = 8\pi r \dot{r}$ for spherical droplets. Combining these relations and using (7), one could obtain

$$r\alpha = \rho/(8\pi u\beta). \tag{9}$$

At a constant temperature, the right-hand side of (9) is a constant, and we come back to (5).

Relation (9) shows that the product must be a function of temperature. A processing of our experimental data shows that it weakly depends on the temperature decreasing with increase in T . For example, at $\Delta T = 10^\circ\text{C}$, the product varies only by 1–2%.

We would like to note that (8) describes the evaporation regime at a constant temperature. This regime could be needed at special technologies of drying. Formula (8) could be applied in the case of evaporation of liquid droplets with a low specific heat of evaporation that is accompanied by a slight variation in the temperature of droplets.

Conclusions

The special method of keeping the constant temperature during the evaporation process of water droplets allowed one to eliminate the cooling effect. It makes possible to study the condensation coefficient and the concentration of vapor near the droplet surface in detail.

From the analysis of experimental data, we have found that the evaporation rate of water droplets considerably depends on the buffer gas. It increases while passing from Ar to Ne, and to He.

We have established the phenomenological relation between the condensation coefficient of water droplets α and their radius r : $r\alpha = \text{const}$. This could explain a considerable dispersion in magnitudes of α obtained by different authors for the same liquid with the help of different methods.

The phenomenological formula (8) for the evaporation rate of water droplets at a constant temperature is proposed that fairly well describes the experimental results in a wide range of pressures (750–15 mm Hg). It takes into account the dependence of the vapor concentration near the droplet surface on a rate of varying its surface. At a constant temperature, this dependence is extrapolated by a linear function with the slope that does not depend on a type of buffer gas. To our mind, it is always true because, actually, the small parameter of expansion is the ratio $\dot{r}/v_T \ll 1$ (the rate of varying the droplet radius to the thermal velocity of vapor molecules). The phenomenological parameter β for a given droplet and a buffer gas depends only on the temperature of evaporation and slowly decreases with increase in the temperature.

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ОСОБЛИВОСТІ ВИПАРОВУВАННЯ КРАПЛИН ВОДИ ПРИ ПОСТІЙНІЙ ТЕМПЕРАТУРІ

В.М. Мальнев, В.М. Нужний, Г.М. Вербінська, О.А. Загородня

Резюме

Проаналізовано експериментальні дані з випаровування краплин води в широкому діапазоні тисків (760–15 мм рт. ст.) при постійній температурі, що забезпечується за допомогою спеціальної методики. Проілюстровано, що при тисках, нижчих за 100 мм рт. ст. (в так званому перехідному режимі випаровування), формули стандартної теорії не узгоджуються з експериментом. Ці неузгодження поглиблюються із зменшенням тиску. Встановлено, що в перехідному режимі випаровування коефіцієнт конденсації води α на поверхні краплі залежить від її радіуса r . Знайдено феноменологічне співвідношення $r \cdot \alpha = \text{const}$. Запропоновано формулу швидкості випаровування краплин при постійній температурі, яка добре описує експериментальні дані в усьому діапазоні тисків, навіть при низьких тисках, коли формули стандартної теорії не працюють.

ОСОБЕННОСТИ ИСПАРЕНИЯ КАПЕЛЬ ВОДЫ ПРИ ПОСТОЯННОЙ ТЕМПЕРАТУРЕ

В.Н. Мальнев, В.М. Нужный, Г.Н. Вербинская, О.А. Загородня

Резюме

Проанализированы экспериментальные данные по испарению капель воды в широком диапазоне давлений (760–15 мм рт. ст.) при постоянной температуре, что обеспечивается с помощью специальной методики. Проиллюстрировано, что при давлениях, ниже 100 мм рт. ст. (в т. н. переходном режиме испарения), стандартные формулы теории не согласуются с экспериментом. Эти расхождения увеличиваются с уменьшением давления. Установлено, что в переходном режиме испарения коэффициент конденсации воды α на поверхности капли зависит от ее радиуса r . Найдено феноменологическое соотношение $r \cdot \alpha = \text{const}$. Предложена формула скорости испарения капель при постоянной температуре, которая хорошо описывает экспериментальные данные во всем диапазоне давлений, даже при низких давлениях, когда формулы стандартной теории не работают.