

EFFECT OF THE MACROSCOPIC PARAMETERS AND COMPOSITION OF THE AMBIENT
ON THE MASS TRANSITION KINETICS OF LIQUIDS

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The kinetics of liquid evaporation in atmospheres of various inert gases is investigated. The specific features of the process and the effect of the temperature, pressure, ambient composition, and the evaporation surface temperature on the liquid evaporation rate are determined.

The evaporation rate under high vacuum conditions ($Kn \geq 1$) is determined by the phase transition kinetics at the surface, so that it depends on neither the velocity of the gas flow nor its composition and is strictly proportional to the evaporation surface area [1], while it depends on the ambient gas composition if $Kn \ll 1$. The considerable influence of the inert gas type on liquid evaporation has been reported in [1-12, etc.], but the results given in these papers and their physical interpretation are to a large extent contradictory. The considerable (up to 100%) discrepancy between the experimentally measured evaporation rates and those predicted theoretically on the basis of diffusion coefficient values that has been found in certain papers can be explained in different ways: by the concentration discontinuity near the liquid surface [5-7], the change in the physicochemical state of the liquid's surface [8], adsorption of inert gas molecules at the evaporation surface [9, 10], the effect of gravitation [11], variation of the surface temperature during the evaporation process [12], etc. Analysis of the literature data suggests that the state of the liquid and the type and partial pressure of the inert gas play a considerable role in the evaporation kinetics, but the trends of these influences are still not clearly understood.

We provide here the results of an experimental investigation of the liquid evaporation kinetics for different thermodynamic parameters of the ambient. The evaporation occurs in a vacuum chamber 1 (Fig. 1), provided with screening panels 2 the temperature of which is varied by pumping either a hot gas or liquid nitrogen through them. An evaporating pan 4, with a diameter of 0.097 m, whose side surfaces are heat-insulated, is placed inside the chamber on scales 3. The liquid under investigation is poured into the pan through tube 5. Heat is supplied to the evaporation surface from an electric heater 6, which is mounted on a special holder under the pan bottom, so that it does not affect weight loss measurements, i.e., the thermal flux necessary for liquid evaporation is supplied by radiation and thermal conductivity through a narrow gap.

A panel 7 with a diameter of 0.18 m, whose temperature can be regulated, is located above the evaporating pan in the parallel palen at a distance of 0.025 m. Thus, the evaporation occurs within the clearance formed by the parallel surfaces of the liquid and panel 7.

Screened copper-Constantan microthermocouples 10 with heads flattened in the isothermal plane are fastened on a coordinate spacer, mounted by means of micrometric screw 8 on the shaft of reversing motor 9. The mean value of the readings of four thermocouples at different points of the surface is used as the surface temperature of the liquid. The partial vapor pressure at various distances from the surface is measured by means of the psychrometric method, based on determining the temperature values by means of two temperature data units (microthermocouples), a "dry" thermocouple and a "wet" one, whose sensing element is wetted by the liquid under investigation and is in thermodynamic equilibrium with the ambient gas [13]. If there is no heat supply to the surface of the "wet" thermocouple, it records the temperature corresponding to the partial vapor pressure at a certain distance

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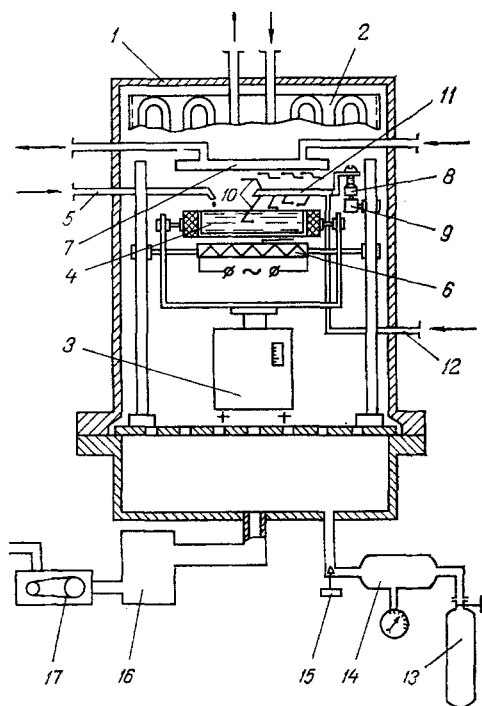


Fig. 1. Schematic diagram of the experimental device.

from the evaporation surface. The moistening of the "wet" thermocouples is effected by means of reservoir 11, to which the investigated liquid is supplied through tube 12. Small wicks are introduced on top; they end in a loop formed by the thermocouple electrodes lying in the isothermal plane. As a result of the capillary potential of the small wicks, the liquid is supplied to the loop and is retained there in the form of a drop, moistening the wick that covers the junction of the "wet" thermocouple. The distance between the thermocouple and the evaporation surface is determined optically with an accuracy to 0.1 mm.

The chamber can be filled with any inert gas from cylinder 13 through a constant-pressure chamber 14 and a valve 15. The evacuation system consists of a BN-4500 booster vacuum pump 16 and a VN-6g mechanical vacuum pump 17.

Distilled water was used as the liquid to be investigated, which was evaporated in atmospheres of helium, nitrogen, carbon dioxide, argon, and Freon-22 under pressures varying from $1.3 \cdot 10^3$ to $6.7 \cdot 10^3$ Pa.

The specific features of the experimental method were the following. The chamber was evacuated to $P = 0.1$ Pa, then cut off from the pumping system, and filled with the gas under investigation to the assigned pressure. The liquid was poured into the evaporating pan through tube 5, and the nitrogen panels 2 and heater 6 were switched on. Thus, in all experiments, the liquid vapor was pumped out solely by freezing it on the nitrogen panels, which were kept at a constant temperature: 223, 213, and 190°K.

In order to reduce the error in measuring the temperature and, thus, the partial vapor pressure, the temperatures of panel 7 and of the evaporation surface were equalized, i.e., the temperature within the clearance was virtually constant. The experiments were performed under steady-state conditions. In order to keep the evaporation surface at a constant temperature, a device for automatic temperature regulation and stabilization was developed, which employed as the heat-sensing elements microthermoresistors with platinum-iridium point contacts, which were held at the evaporation surface. The control accuracy was as high as 0.2°.

The described method made it possible to determine the effect of the type of the inert gas in the chamber on the liquid evaporation rate j_m by direct measurement of the mass loss in the process of evaporation.

It should be noted that, for many binary mixtures used in experiments, the literature does not provide reliable experimental values of the diffusion coefficient in the temperature range from 275 to 283°K. Therefore, in processing the experimental data, the calculations for each binary mixture were performed with respect to the two most reliable values

TABLE 1. Parameters of the Intermolecular Interaction Potential of Binary Gas Mixtures

Substance	M, kg/mole	$\sigma, \text{ \AA}$	$\epsilon/k, K$	Binary mixture, H ₂ O + gas		Literature source
				$\sigma_{12}, \text{ \AA}$	$\epsilon_{12}/k, K$	
Helium	4,003	2,551	10.22	2,596	90,93	[15]
Nitrogen	28,013	3,798	71.4	3,167	240,35	[15]
Argon	39,948	3,542	93.3	3,058	274,75	[15]
Same	39,948	3,465	116.0	3,030	209,95	[14]
Carbon dioxide	44,010	3,941	195.2	3,226	397,40	[15]
Freon-22	86,469	4,620	267.3	3,490	465,02	[15]*
Same	86,469	4,580	276.9	3,480	473,30	[15]†
Water	18,015	2,641	809.1			[15]
Same	18,015	2,650	380.0			[14]

The σ and ϵ/k values for Freon-22 were calculated by means of the alternative Brokaw method [15]: *, with respect to the critical parameters of the substance: †, with respect to the boiling parameters [14].

of D_{12} , obtained by linear extrapolation of the experimental results, calculation based on the kinetic theory of gases, or semiempirical correlation of experimental data, which, according to estimates [14, 15], provides the best approximation of the experimental results. The parameters of the potential of intermolecular interaction in binary gas systems are given in Table 1.

On the basis of our investigations, we have found that the j_m values for water in atmospheres of helium, nitrogen, and carbon dioxide are in the ratio of 15:6:4. Similar results were obtained in [2] for water evaporating in atmospheres of hydrogen, nitrogen, and carbon dioxide, but in our experiments on evaporation in a rarified gas, the ratio of rates was higher than in [2]. Thus, the j_m value for water in helium exceeds by a factor larger than 3.5 the j_m value in nitrogen, and by a factor of 4.5 in Freon-22, all other conditions being equal and for a constant evaporation temperature, while, in [2], the water evaporation rate in hydrogen, which has a smaller molecular weight in comparison with helium, exceeds the evaporation rate in nitrogen by a factor of only 1.7.

This discrepancy can be explained by the failure to account in [2] for the variation of the liquid temperature during the evaporation process in various inert gases. Actually, the diffusion coefficient increases with a reduction in the molecular weight of the gas, which leads to an increase in j_m and, thus, for a constant thermal flux, a reduction in the temperature of the liquid due to a change in its enthalpy, which, in turn, reduces the evaporation rate.

It is evident from Fig. 2a that j_m diminishes with a decrease in T_g ; the lower the ambient pressure and the molecular weight of the inert gas, the greater the effect of temperature on the evaporation rate. Thus, for $P = 1.2 \cdot 10^3$ Pa, a 1° change in T_g causes a 15% change in the water evaporation rate in helium, and a change of 10% if $P = 6.7 \cdot 10^3$ Pa. Thus, the liquid temperature is one of the main determining factors in investigating the evaporation kinetics, interpreting the experimental results, and comparing them with the results obtained by other researchers.

The liquid evaporation rate increases sharply with a reduction in the ambient pressure (Fig. 2b). For $T_g = \text{const}$, as P increases to a value above $2.7 \cdot 10^3$ Pa, the experimental points are approximated satisfactorily by a straight line, i.e., it can be considered with sufficient accuracy that j_m is inversely proportional to the ambient pressure in the investigated range of surface temperatures, which is characteristic for the diffusion process. With an increase in the evaporation rate (this corresponds to a reduction in the ambient pressure in our case), the dependence $j_m = j_m(1/P)$ deviates from linearity, which is especially noticeable during water evaporation in a helium atmosphere. This can be explained by the convective flow caused by evaporation that is due to the gradient in the concentration of the inert gas and is proportional to the ratio of the barometric pressure to the partial gas pressure [16] (Stefan's convective flow), i.e., vapor removal from the evaporation surface occurs as a result of both molecular diffusion and molar relationships.

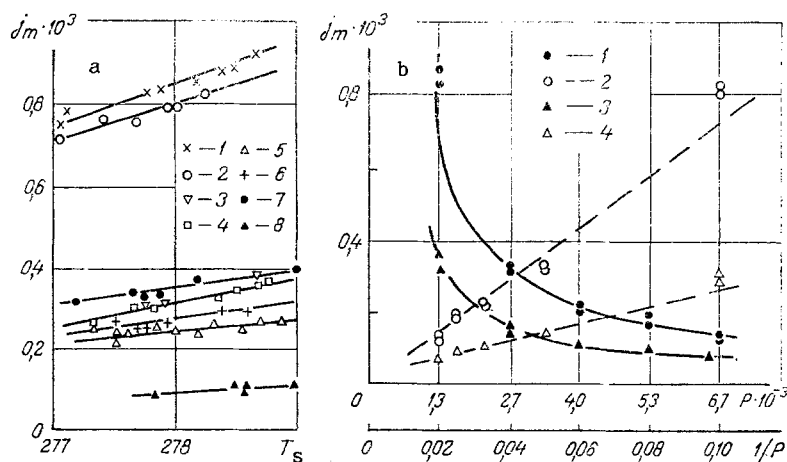


Fig. 2. Water evaporation rate j_m (kg/m²·sec) as a function of a) the temperature of the evaporation surface (°K); b) ambient pressure (Pa) (solid curves) and $1/P \times 7.5 \cdot 10^{-3}$ (dashed curves) for evaporation in an inert gas ambient: a) 1) helium; 3) nitrogen; 4) argon; 5) carbon dioxide; 6) Freon-22 at the ambient pressure $P = 1.3 \cdot 10^3$ Pa and for the outer screen temperature $T_{op} = 223^\circ\text{K}$; 7) helium ($2.7 \cdot 10^3$ Pa; 223°K); 8) nitrogen ($5.3 \cdot 10^3$ Pa; 223°K); 2) helium ($1.3 \cdot 10^3$ Pa; 190°K); b) 1) and 2) helium 3) and 4) nitrogen at $T_s = 278^\circ\text{K}$ and $T_{op} = 223^\circ\text{K}$.

The experimental results were used for calculating the diffusion flow proper and the diffusion flow with an allowance for the Stefan correction accounting for the differences between the partial vapor pressures measured simultaneously by means of differential and ordinary thermocouples at different distances from the evaporation surface. Satisfactory mutual agreement and reproducibility of the results of these calculations were observed. Comparison between the theoretical values of the mass flow and the values obtained in experiments has shown that vapor removal from the evaporation surface in a rarefied ambient actually occurs as a result of diffusion flow with an allowance for the Stefan correction.

The smaller the molecular weight of the inert gas in which evaporation takes place, the higher the j_m value. For $T_s = \text{const}$, j_m is proportional to $M_2^{0.5}$, inversely proportional to the mean molecular weight of the vapor-gas mixture \bar{M} , which accounts for the relationship between the components in the mixture [1], and inversely proportional to the reduced molecular weight of the mixture $\bar{M} = M_1 M_2 / (M_1 + M_2)$ with the power of 0.85. It is known [14] that \bar{M} to the power of -0.5 appears in the expression for the diffusion coefficient of a binary mixture obtained by the method of successive approximations within the framework of the gas kinetics theory. However, the parameter σ_{12} of the potential function characterizing the size of interacting molecules and the collision integral $\bar{\Omega}_D$, which appear in the expression for the diffusion coefficient, and also depend on \bar{M} . By using the hydrodynamic representation of diffusion processes, it was found in [1] that the collision integral is proportional to $\bar{M}^{0.5}$, and the diffusion coefficient should be inversely proportional to \bar{M} . If a higher-order approximation is used for D_{12} , it can be assumed that the effect of \bar{M} on D_{12} and, thus, on j_m will be somewhat different from that found in experiments.

The dependence of j_m on $\ln(P - P_{s1}) / (P - P_s^*)$ (Fig. 3) was calculated on the basis of the assumption that the condition of thermodynamic equilibrium is satisfied at the evaporation surface, i.e., it was assumed that the vapor pressure at the phase interface P_s^* is equal to the saturation pressure P_{sv} corresponding to the temperature of the phase transition surface. Comparison between these relationships and experimental data has shown that there is good agreement for $T_s = \text{const}$ and $P = (2.7 - 6.7) \cdot 10^3$ Pa for water evaporation in helium, while, with an additional increase in $\ln(P - P_{s1}) / (P - P_s^*)$, i.e., an increase in the evaporation rate (corresponding to $P < 2.7 \cdot 10^3$ Pa in our investigations), the experimentally determined evaporation rate is lower than the theoretical rate by approximately 40%. A certain amount of scatter of the points can be explained by the fact that the diagram contains points for three different values of the external panel temperatures (cf. curves 1 and 2 in Fig. 2a).

A certain increase in j_m in comparison with the theoretical value is observed for water evaporating in nitrogen and Freon-22 (roughly 40% for Freon-22), while good agreement be-

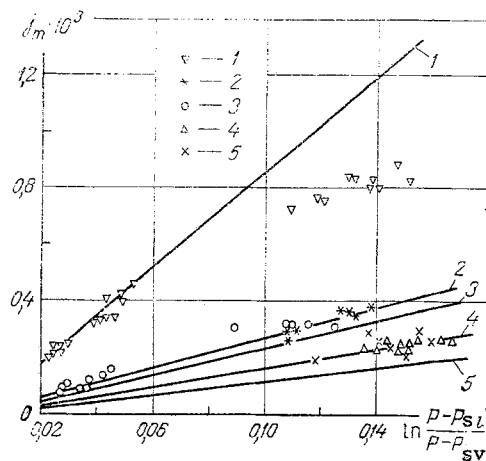


Fig. 3. Evaporation rate j_m ($\text{kg}/\text{m}^2 \cdot \text{sec}$) as a function of $\ln(P-P_s L)/(P-P_s^*)$, calculated on the basis of diffusion kinetics with an allowance for the Stefan flow (solid curves) and determined experimentally (points) for water evaporating in different ambients. 1) Helium; 2) argon; 3) nitrogen; 4) carbon dioxide; 5) Freon-22.

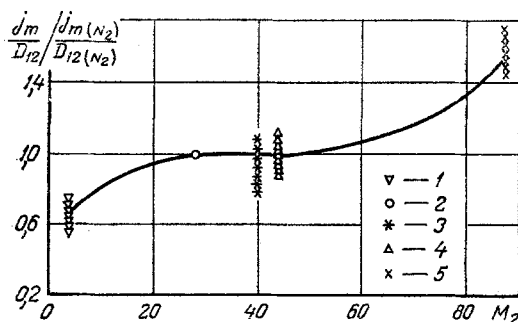


Fig. 4. Reduced water evaporation rate, related to the reduced water evaporation rate in nitrogen, as a function of the molecular weight of the inert gas M_2 (kg/kmole).

tween these values if found for evaporation in carbon dioxide and argon. This trend holds for both diffusion coefficients used in calculating diffusion flows.

The lower value of j_m for water in helium in comparison with the theoretical value confirms the results obtained in [9, 10, 12]. The reduction of j_m mentioned in [12] was not observed for other gases. Our experiments were performed at $T_s = \text{const}$, while the lower rate of water evaporation for all gases except a mixture of butane and propane in [12] can be explained by a reduction in the evaporation surface temperature, with a reduction in pressure and the adsorption of inert gas monolayers.

The relationship between the reduced evaporation rate j_m/D_{12} and the molecular weight of the inert gas, calculated in a manner similar to that in [9], shows (Fig. 4) that, in comparison with nitrogen, helium retards, while Freon-22 accelerates, the evaporation process. Carbon dioxide and argon affect the evaporation rate only through the diffusion coefficient, in contrast to the results from [8, 9], where a considerable (up to 80%) increase of the evaporation rate in a carbon dioxide ambient was found in comparison with the rate determined on the basis of the diffusion coefficient.

Analyzing our results, comparing them with those found in the literature, and checking the hypotheses suggested for their interpretation, we reached the conclusion that the contradictions in the theory of liquid evaporation in various inert gases are most probably due to an incorrect treatment of the experimental results and failure to take into account in calculations the density and temperature discontinuities near the evaporation surface, the values of which increase with a reduction in pressure and an increase in the mass flow from the evaporation surface [17].

Discrepancies between the experimental and theoretical values of the evaporation rate appear as the pressure is lowered. An estimate provided in correspondence with [18] has shown that, even for $P < 2.7 \cdot 10^3$ Pa and a considerable evaporation rate ($j_m > 6 \cdot 10^{-4}$ kg/m²·sec), the density jump exceeds the experimental error, which starts to affect the calculation results. Therefore, the equilibrium condition $P_S^* = P_{SV}$ used in calculations (Fig. 3) leads to an increase in the $\ln(P - P_S)/(P - P_S^*)$ value and, thus, an increase in the diffusion mass flow in comparison with experimental data. By equating the experimental and theoretical rates of water evaporation in helium at $P = 1.3 \cdot 10^3$ Pa and determining P_S^* , we find that the partial pressure jump near the evaporation surface is equal to 13 Pa, which agrees with an accuracy to 20% with the value $(P_{SV} - P_S^*)$ measured in experiments at a distance from the evaporation surface equal to the thickness of the thermocouple junction. By substituting this value in the Hertz-Knudsen equation for j_m , we find the value of 0.04 for the water evaporation coefficient, which agrees with the values given in the literature [2, 19].

In experiments on water evaporation in carbon dioxide, it was found that carbon dioxide is readily adsorbed on various cooled surfaces, probably including the evaporation surface. However, we did not find that j_m was influenced by this adsorption, let alone absorption of carbon dioxide bubbles by water, which was observed in [8].

It follows from the above that, for liquid evaporation in inert-gas ambients and for small Knudsen numbers ($Kn \ll 1$), i.e., in the diffusion region, the evaporation rate can be calculated with an accuracy sufficient for practical purposes on the basis of diffusion kinetics with an allowance for the Stefan flow, assuming a quasiequilibrium process. As the ambient pressure decreases and the mass flow from the evaporation surface increases, it becomes necessary to account for the concentration and temperature jumps near the surface in calculating the evaporation rate.

NOTATION

T_S and T_{op} , temperatures of the evaporation surface and of the outer nitrogen panels, respectively (°K); P and P_{SV} , ambient pressure and vapor saturation pressure, respectively (Pa); P_S^* and $P_S \bar{l}$, partial vapor pressures at the interface of phases and at the distance \bar{l} from the evaporation surface (Pa), respectively; j_m , evaporation rate (kg/m²·sec); D_{12} , diffusion coefficient (m²/sec); M , molecular weight (kg/kmole); $\bar{M} = M_1 M_2 / [M_1 + (M_2 - M_1) c_1]$ and $\bar{M} = M_1 M_2 / (M_1 + M_2)$, mean and reduced molecular weights of the vapor-gas mixture, respectively; c , concentration, σ_{12} and Ω_D , collision diameter and collision integral, respectively; ϵ/k , reduced temperature; Kn , Knudsen number. Subscripts: 1, vapor; 2, inert gas.

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CONDENSATION ENLARGEMENT OF AEROSOL PARTICLES WHEN A GAS MIXES
WITH A VAPOR

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From the equations of material and heat balances of the process, functions are obtained for determining the amount of condensate and the diameter of the aerosol particles following the mixing of a gas with a vapor.

The condensation enlargement of aerosol particles in the mixing of a gas with a vapor is used to increase the efficiency of separation of mechanical impurities in the scrubbing of industrial exhaust gases and ventilating air [1-6]. The use of this method enables one not only to separate finer particles from the gas than under ordinary conditions, but it also considerably reduces the energy expended on scrubbing.

To start the condensation process in a two-phase system it is necessary to create supersaturation greater than the critical value determined by the Kelvin equation [7]:

$$S_{cr} = \frac{p_d}{p_s} = \exp \left(\frac{4\sigma M_v}{RT_m \rho_c d_i} \right). \quad (1)$$

We note that Eq. (1) is valid in vapor condensation both onto liquid drops and onto solid particles, since the mechanism of the process is the same in both cases [7].

To determine the diameter of the aerosol particles after mixing we analyze the equations of material and heat balances of the process. Here we make the following assumptions: The volume of the aerosol particles and of the condensate formed is small compared with the volume of the vapor-gas mixture, the temperature of the particles and condensate after mixing equals the temperature of the mixture, the mixing takes place without heat exchange with the surrounding medium, and the gas and vapor obey the laws of an ideal gas.

The equation of heat balance, analogous to that presented in [8] but with allowance for the initial moisture content of the gas, can be written in the form

$$G_g c_g (T_m - T_g) + x_i G_g c_v (T_m - T_g) = G_v c_v (T_v - T_m) + G_c r. \quad (2)$$

Dividing Eq. (2) by G_g and introducing the notation $k = G_c/G_g$ and $\Delta x = G_v/G_g$, after transformations we obtain

$$(c_g + x_i c_v) (T_m - T_g) = \Delta x c_v (T_v - T_m) + kr. \quad (3)$$

We represent the equation of material balance in the form

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