

DETERMINATION OF THE ONSAGER KINETIC COEFFICIENTS DESCRIBING THE DIFFUSION PROCESSES BY EXPERIMENTAL DATA ON EVAPORATION OF WATER DROPLETS

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On the basis of irreversible thermodynamics, we have obtained the analytical expression for the vapor diffusion flux on the evaporation of droplets in the diffusion mode. A method to find Onsager phenomenological coefficients defining the diffusion coefficient is proposed. Using the obtained theoretical expressions, we have analyzed the experimental data on the water droplet evaporation into a gas-vapor mixture (water vapor and buffer gas), where He, CH₃, Ne, air, Ar, CO₂ were used as buffer gases. The experiments were executed at temperatures of 283 and 293 K and relative humidities of 53 and 75%.

1. Introduction

The consideration of the quasistationary diffusion mode of evaporation of a liquid droplet into a binary gaseous mixture of the droplet substance vapor and a buffer gas involves usually the first Fick equation [1]

$$J_1 = -4\pi r^2 D \frac{d\rho}{dr}, \quad (1)$$

where ρ is the mass density of the droplet substance vapor in a gas-vapor mixture, r is the distance from the droplet center, and J_1 is the mass diffusion flow of the droplet substance vapor through the sphere surface with area $4\pi r^2$. The kinetic coefficient of interdiffusion D used in Eq. (1) is considered to depend only on the temperature of the medium, the type of components of the mixture, and the pressure of a gas-vapor mixture and is calculated by methods of the kinetic theory of gases. However, the modern experimental and theoretical data [2–4] testify that the coefficient of interdiffusion depends on the concentrations of components of a gas-vapor mixture. Therefore, it is necessary to take this dependence into account for a more correct description of the process of evaporation of a droplet in the diffusion mode. It is worth noting that, in nonequilibrium thermodynamics, the force conjugate to a diffusion flow is the gradient of the

chemical potential μ of a diffusing substance (see [5] and references therein), rather than the gradient of its mass density ρ .

2. Derivation of a Working Formula and Its Analysis

According to the phenomenological linear theory of nonequilibrium processes, the formula for a thermodynamic flow can be given as $J_i = \sum_{k=1}^n L_{ik} X_k$ where J_i is the thermodynamic flow of a certain physical quantity, X_k is the thermodynamic force conjugate to the k -th flow, and L_{ik} are the phenomenological Onsager coefficients [6].

On the consideration of the evaporation of a droplet, the formula for a diffusion flow of vapor can be presented in the general case by the following formula including the direct and cross effects [6]:

$$\vec{J}_i = -L_{iq} \frac{1}{T^2} \vec{\nabla} T - \sum_{j=1}^n L_{ij} \vec{\nabla} \frac{\mu_j}{T}. \quad (2)$$

Here, \vec{J}_i is the diffusion flow of the i -th component into the mixture, μ_j is the chemical potential of the j -th component of the mixture, L_{ij} are the phenomenological Onsager coefficients, and L_{iq} is the phenomenological Onsager coefficient responsible for the cross effects between the heat flow and the mass flow of the i -th component of the mixture.

Directly in the executed series of experiments, we have realized the mode of thermostatic control over a droplet: its temperature was held to be equal to the temperature of a gas-vapor mixture. For the given choice of conditions of the experiment, we consider that the heat flow to the droplet surface is absent. In view of the absence of both the heat flow to the droplet surface and the temperature gradient and by

neglecting the cross terms, we can reduce Eq. (2) to the form

$$\vec{J}_1 = -L_{11} \text{grad} \frac{\mu_1}{T}, \quad (3)$$

where \vec{J}_1 is the diffusion flow of the droplet substance vapor into the mixture, L_{11} is the Onsager phenomenological coefficient, and μ_1 is the chemical potential of unit mass of the droplet substance vapor in the gas-vapor mixture. Assuming the mixture to be ideal, we can present μ_1 in the form [7]

$$\mu_1 = \mu_{01}(T, P) + \frac{RT}{M_1} \ln(n_1), \quad (4)$$

where μ_{01} is the chemical potential of the pure substance (water vapor) per unit mass, n_1 is the relative molar concentration of the droplet substance vapor in the mixture, M_1 is the molar mass of the droplet substance vapor, T is the temperature, P is the pressure in the mixture, and R is the gas constant.

Passing in relation (4) from the relative molar concentration to the relative mass one, we obtain the formula

$$\mu_1 = \mu_{01}(T, P) + \frac{RT}{M_1} \ln\left(\frac{c_1 M_2}{c_1 M_2 + (1 - c_1) M_1}\right), \quad (5)$$

where c_1 is the relative mass concentration of the droplet substance vapor in the mixture, and M_2 is the molar mass of a buffer gas.

Since the problem possesses the spherical symmetry, we can integrate over the angles. Taking into account the fact that P and T are invariable, we get the following formula for a diffusion flow of vapor:

$$\begin{aligned} J_1 &= -4\pi r^2 L_{11} \frac{1}{T} \frac{\partial \mu_1}{\partial r} = \\ &= 4\pi r^2 L_{11} R \frac{1}{c_1(c_1 M_2 + (1 - c_1) M_1)} \frac{\partial c_1}{\partial r}. \end{aligned} \quad (6)$$

Equation (6) is supplemented with the boundary conditions

$$\begin{cases} c_1(r = R_k) = c_{10}, \\ c_1(r = \infty) = c_{1\infty}, \end{cases} \quad (7)$$

where c_{10} is the relative mass concentration of vapor above the droplet surface, and $c_{1\infty}$ is the relative mass concentration of vapor at infinity.

Integrating expression (6) with regard for the boundary conditions (7), we obtain

$$\begin{aligned} J_1 &= \frac{4\pi R_k L_{11} R}{M_1} \ln\left(\frac{c_{1\infty}(M_1 - c_{10}(M_1 - M_2))}{c_{10}(M_1 - c_{1\infty}(M_1 - M_2))}\right) = \\ &= \frac{4\pi R_k L_{11} R}{M_1} \ln\left(\frac{\rho_{10}}{\rho_{1\infty}}\right). \end{aligned} \quad (8)$$

In view of the connection between the mass flow of a droplet substance and the rate of variation of the droplet surface area, we obtain

$$\frac{dS}{dt} = \frac{8\pi L_{11} R}{M_1 \gamma} \ln\left(\frac{\rho_{10}}{\rho_{1\infty}}\right), \quad (9)$$

where $\frac{dS}{dt}$ is the absolute value of the rate of variation of the droplet surface area determined in the experiment, γ is the density of a droplet substance, ρ_{10} is the mass density of vapor above the droplet surface, and $\rho_{1\infty}$ is the mass density of vapor at infinity. We rewrite relation (9) for L_{11} in the form

$$L_{11} = \frac{dS}{dt} \frac{M_1 \gamma}{8\pi R} \ln\left(\frac{\rho_{10}}{\rho_{1\infty}}\right). \quad (10)$$

This formula allows us to determine L_{11} from experimental data on the evaporation of droplets. Here, we use (10) in the calculations of values of the Onsager coefficients from the experimental data on the evaporation of water droplets in the interval of pressure from 750 down to 325 mmHg. In this interval of pressure, the Knudsen number [1, 8] remains small for the whole stage of quasistationary evaporation, which testifies that the rate of evaporation in this interval of pressure is defined exclusively by the diffusion removal of vapor. Thus, we may consider that relation (10) describes completely the rate of evaporation of a droplet in this interval of pressure.

By analyzing relation (6) for a diffusion flow, we can separate two parts in the term which includes explicitly the coefficient of interdiffusion: the kinetic part of the coefficient of diffusion, i.e. the Onsager coefficient, and the equilibrium part related to the equation of state of a mixture. As seen from (6), the equilibrium part of the coefficient of interdiffusion is a function which depends on the relative mass concentration of the droplet substance vapor and its molar mass, as well as on the molar mass of the buffer gas of a gas-vapor mixture.

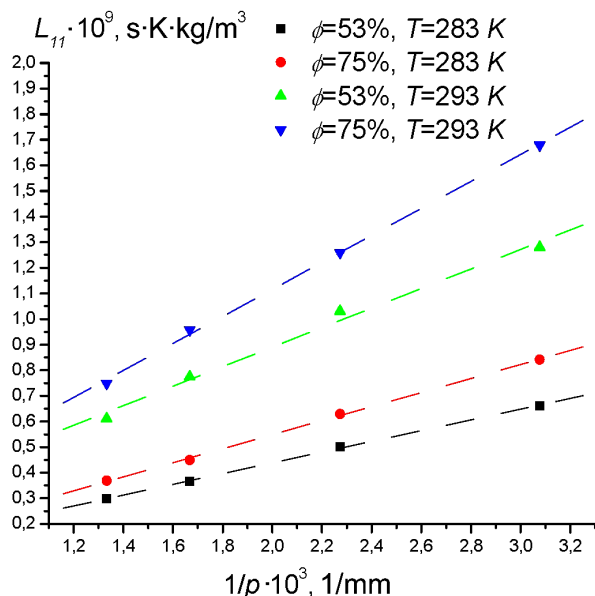


Fig. 1. Onsager phenomenological coefficient versus the inverse pressure in a gas-vapor mixture of water vapor and argon at temperatures of the mixture of 283 and 293 K and relative humidities of 53 and 75%

3. Description of the Method of the Experiment

The experimental rates of variation of the droplet surface area under various experimental conditions were determined with the help of the following experimental method.

The droplets under study were hanged up on a suspension at the center of a thermostating chamber, in which constant temperature and pressure were held. The measurement of the droplet surface area in the process of evaporation was executed in equal time intervals with the help of the photographing. It was realized with a web-chamber mounted before a glass window in the longitudinal part of the chamber in front of a suspension, on which a droplet was positioned. Near the suspension, two vertical scaling wires with a known diameter were positioned. The photos of a droplet with scaling wires were processed with a program which approximates the image of a droplet with a circle and determines the diameter and the area of a droplet at the given time moment.

In the experiment, we measured directly the droplet surface area S in certain time intervals. Then we constructed the function $S(t)$ which has the form of

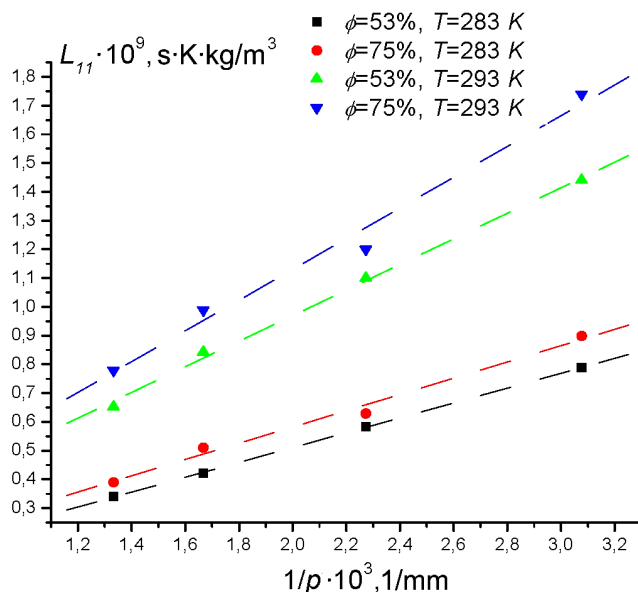


Fig. 2. Onsager phenomenological coefficient versus the inverse pressure in a gas-vapor mixture of water vapor and air at temperatures of the mixture of 283 and 293 K and relative humidities of 53 and 75%

a straight line on a certain time interval, so that we determined the slope angle tangent $\frac{dS}{dt}$ of the straight line.

4. Analysis of Experimental Data

By using relation (10), we calculated values of the Onsager kinetic coefficient which enters the formula for the coefficient of diffusion. The presented dependences of the Onsager coefficient on the inverse pressure ($1/p$) were calculated from the obtained experimental values of $\frac{dS}{dt}$ under various conditions of the experiment. In particular, we constructed the dependences $L_{11}(1/p)$ for different buffer gases and at various values of the temperature of a mixture and relative humidities (for different ratios of the density of water vapor at infinity to the density of saturated water vapor at the temperature of a mixture).

In Figs. 1 and 2, we give the obtained dependences of the Onsager coefficient $L_{11}(1/p)$ for a gas-vapor mixture of water vapor and argon (Fig. 1) or air (Fig. 2) for the temperatures of the mixture equal to 283 and 293 K and relative humidities of 53 and 75%. The analysis of the data given in the plots showed that the values of L_{11} at fixed pressure and temperature of the mixture, but for

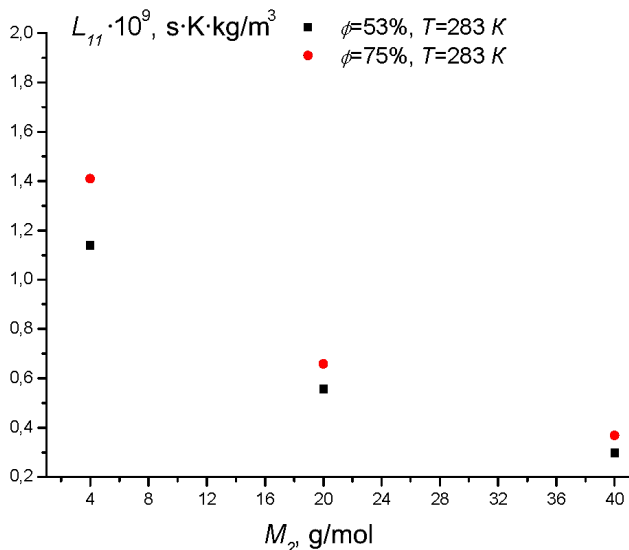


Fig. 3. Onsager phenomenological coefficient versus the molar mass of a buffer gas in a gas-vapor mixture of water vapor and an inert gas (helium, neon, argon) at temperatures of the mixture of 283 and 293 K and relative humidities of 53 and 75% at a pressure in the mixture of 750 mmHg

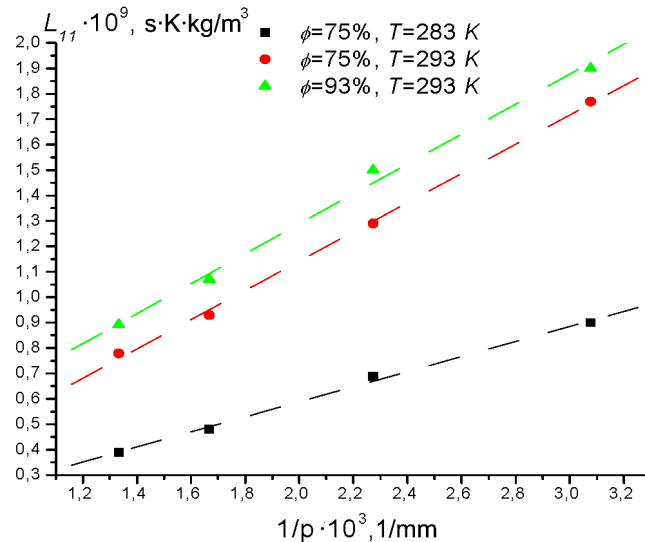


Fig. 5. Onsager phenomenological coefficient versus the inverse pressure in a gas-vapor mixture of water vapor and methane at temperatures of the mixture of 283 and 293 K and relative humidities of 75 and 93%

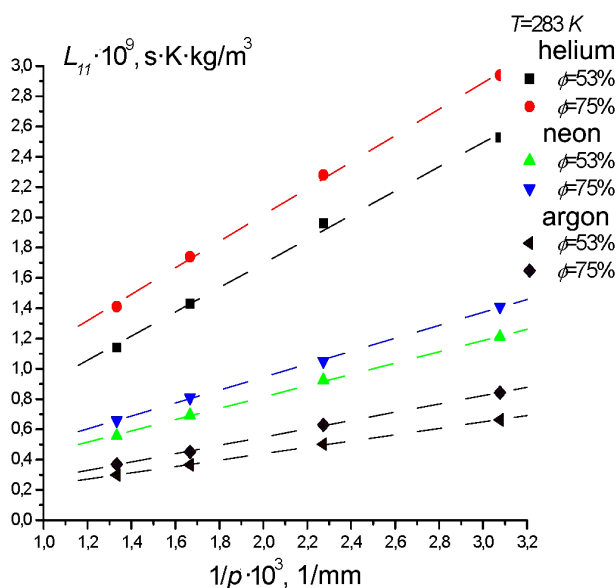


Fig. 4. Onsager phenomenological coefficient versus the inverse pressure in a gas-vapor mixture of water vapor and an inert gas (helium, neon, argon) at a temperature of the mixture of 283 K and relative humidities of 53 and 75%

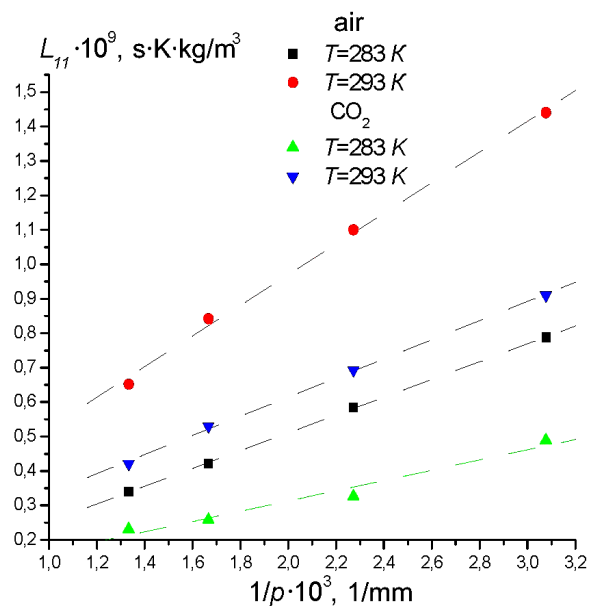


Fig. 6. Onsager phenomenological coefficient versus the inverse pressure in a gas-vapor mixture of water vapor and a buffer gas (air and CO_2) for a relative humidity of 53% and at temperatures of the mixture of 283 and 293 K

different values of the humidity differ from one another. The difference of the values of L_{11} decrease with decrease in the temperature of the mixture.

In Fig. 3, we present L_{11} versus the molar mass of the buffer gas at a temperature of 283 K and a pressure of 750 mmHg in the mixture and at relative humidities

of 53 and 75%. The analysis of these plots indicates that the difference between the values of L_{11} for different humidities at fixed values of pressure and temperature in the mixture decreases with increase in the molar mass of a buffer gas. In turn, the dependences $L_{11}(1/p)$ given in Fig. 4 show that this decrease in the difference is observed in the whole interval of pressure, for which the processing of experimental data was carried out.

5. Results and Conclusions

1. We have obtained the analytic formula for a diffusion flow of vapor of the substance of a droplet. The formula includes the phenomenological Onsager coefficient L_{11} as a fitting parameter.

2. We have calculated L_{11} for various conditions of experiments and have constructed the plots of L_{11} versus the inverse pressure ($1/p$) for various values of temperature and humidity and different buffer gases.

3. By analyzing the calculated dependences $L_{11}(1/p)$, we have revealed the difference between the values of L_{11} for different values of humidity in a mixture for other fixed conditions of the experiment (pressure, temperature, and the same buffer gas). This difference decreases in the case of fixed buffer gas and pressure, as the temperature of the mixture decreases and the molar mass of the buffer gas increases at given values of the temperature and pressure of the mixture.

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ВИЗНАЧЕННЯ КІНЕТИЧНИХ КОЕФІЦІЄНТІВ ОНЗАГЕРА, ЩО ОПИСУЮТЬ ДИФУЗІЙНІ ПРОЦЕСИ, З ЕКСПЕРИМЕНТАЛЬНИХ ДАНИХ ПО ВИПАРОВУВАННЮ КРАПЕЛЬ ВОДИ

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Резюме

В роботі, виходячи з термодинаміки нерівноважних процесів, отримано аналітичні вирази для дифузійного потоку пари при випаровуванні крапель в дифузійному режимі. Запропоновано метод по визначенню кінетичних коефіцієнтів Онзагера, що визначають коефіцієнт дифузії. З використанням одержаних теоретичних виразів проведено аналіз експериментальних даних по випаровуванню крапель води в парогазову суміш, де в ролі фонового газу виступали: гелій, метан, неон, повітря, аргон та вуглекислий газ, при температурах $T = 283$ К та $T = 293$ К та відносних вологостях 53% та 75%.