HEAT AND MASS TRANSFER IN DISPERSE AND POROUS MEDIA

ABSORPTION OF AMMONIA BY MOVING DROPS OF WATER

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Laboratory experiments were carried out and a theoretical description of the absorption of gaseous ammonia by water drops has been suggested. A mathematical model takes into account the evaporative cooling of drops, Henry's law, and experimental data on the value of Henry's constant. A comparison between experimental and predicted results has been made. At a fixed flow rate of water it is shown that absorption increases with decrease in the radius of drops and their velocity.

Introduction. Ammonia is the gas most widely used in various branches of industry. Its leakage leads to unfavorable ecological situations, as well as irreversible consequences for a technological process, especially in the semiconductor industry [1, 2]. The delivery of water to the zone of evolution of ammonia decreases the concentration of the latter due to gas absorption by water drops. At the present time, the effectiveness of this method of combating ammonia ejections is determined only experimentally with the aid of full-scale plants. Calculations show that a rather large number of parameters [2] influence the effectiveness of ammonia absorption on water drops, especially at its high concentrations in the gas phase, which makes the analysis of natural experiments difficult.

To gain a deeper understanding of this problem, we have carried out laboratory experiments and developed a new mathematical model of absorption which is based on the results of studying evaporative cooling of drops [3], Henry's law [4, 5], and on the data of experiments [6]. A qualitative analysis of the mathematical model was made which confirms the conclusions drawn in [2]. A comparison of the results of numerical calculations with the data of a laboratory experiment was performed.

Experimental. The experimental setup is shown schematically in Fig. 1. The setup is intended for obtaining the products of ammonia absorption from ammonia-air mixtures by water or other liquid agents. It is a vertical absorption column fitted with equipment for supplying ammonia and air and removing the ammonia-air mixture. The elements of the laboratory setup were assembled on a structure made from metal angles.

The active zone of the column consists of a glass tube 30 mm in diameter and 1.2 m in height in the upper part of which there is a batcher for water and in its lower part a collector for an adsorbate. The batcher (a 250-ml separating funnel) is fitted with a capillary in the lower part with an output diameter of 1.2 mm; it is filled with distilled water. The water supply rate is determined by the number of falling drops; under the conditions of the experiment it ranges from 50 to 120 drops per minute. The receiving part of the column contains a 150-ml beaker for a water solution of ammonia. Air and ammonia are supplied into the absorption column from a cylinder through a reducing valve. The rate of air supply from cylinders 2 and 4 is regulated by gas valves 8 and 10 and controlled by flowmeters 11 and 13. Ammonia is fed from cylinder 3, and the flow rate is regulated with the aid of valve 9 and flowmeter 12.

The size of drops is determined with the aid of a beaker installed in the receiver; the beaker is preliminarily weighted and then filled with 100 drops. The concentration of ammonia in the solution was determined by a standard

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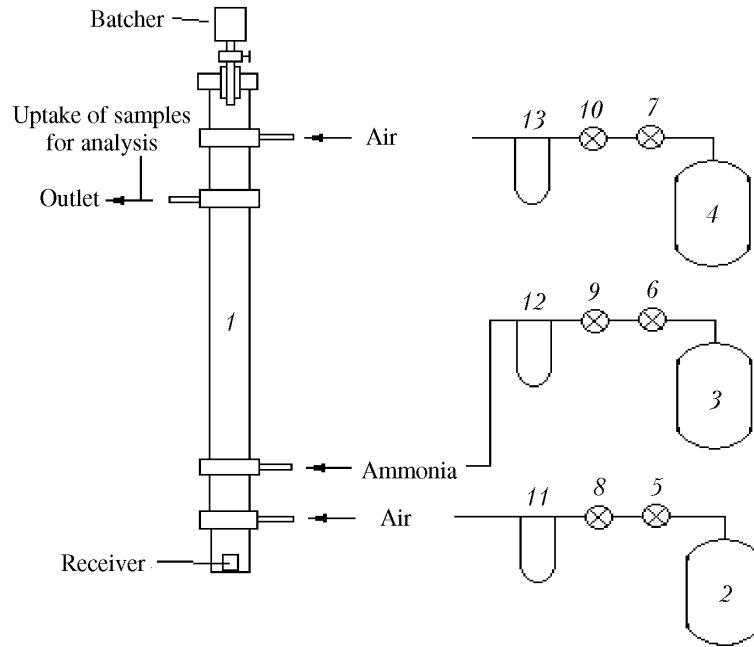
Fig. 1. Schematic diagram of experimental setup: a) absorption column; 2, 4) cylinders with compressed air; 3) cylinder with compressed ammonia; 5, 6, 7) pressure regulators; 8, 9, 10) fine-regulation gas valves; 11, 12, 13) flow meters.

chemical (titrometric) method, and in the ammonia-air mixture it was determined by a KhOBBIT-T-NH_3 gas analyzer or an analyzer of a similar class. Sampling was made from the outlet of the absorption column.

Mathematical Model. In the approximation of a constant density of ammonia vapor the mathematical model of the absorption of ammonia on a water drop moving in the direction opposite to that of a gas mixture consists of a system of ordinary differential equations.

The change in the horizontal and vertical positions of the drop is described by the equations

$$\frac{dx}{dt} = v_x, \tag{1}$$

$$\frac{dz}{dt} = v_z, \tag{2}$$

whereas a change in the velocity of spherical drops [3] under the action of the resistance force gravity is represented by the equations

$$\frac{dv_x}{dt} = -0.5 C_d (\text{Re}) \frac{\pi R^2 \rho}{m} |\mathbf{v}| v_x, \tag{3}$$

$$\frac{dv_z}{dt} = -g - 0.5 C_d (\text{Re}) \frac{\pi R^2 \rho}{m} |\mathbf{v}| v_z. \tag{4}$$

The velocity modulus $|\mathbf{v}|$ is calculated as follows: $|\mathbf{v}| = (v_x^2 + (v_z - u)^2)^{0.5}$. The Reynolds number of a gas flow around a drop is defined as $\text{Re} = 2R\rho |\mathbf{v}|/\mu$. The resistance coefficient $C_d(\text{Re})$ decreases with increase in the Reynolds number [3] and is equal to $C_d(\text{Re}) = \frac{24}{\text{Re}}\left(1 + \frac{\text{Re}^{2/3}}{6}\right)$.

The change in the drop radius R due to evaporation and the change in its temperature T_d in phase transition, absorption, and heat exchange with air [3] are described by the equations

$$\frac{dR}{dt} = \gamma\,(\mathrm{Re})\,\frac{\rho - \rho_s\,(T_d)}{\rho_w} \tag{5}$$

and (in the approximation of a weak solution) by

$$\frac{dT_d}{dt} = \frac{4\pi R^2}{mc}\,\alpha\,(\mathrm{Re})\,(T - T_d) - \frac{3\,(cT - U)}{cR}\,\frac{dR}{dt} + \frac{U_{am}}{mc}\,\frac{dM_{am}}{dt}. \tag{6}$$

It is evident that the temperature of the drop decreases during evaporation of the latter, whereas absorption of ammonia leads to an increase in its temperature. Here, for the absorption of ammonia by water the condition $U_{am} \ll U$ holds. The mass transfer coefficient $\gamma(\mathrm{Re})$ is equal [3] to $\gamma(\mathrm{Re}) = D_w(2 + 0.5\mathrm{Re}^{0.5})/2R$. By analogy between the processes of heat- and mass transfer the heat transfer coefficient of the drop $\alpha(\mathrm{Re})$ is defined by the expression $\alpha(\mathrm{Re}) = \lambda(2 + 0.5\mathrm{Re}^{0.5})/2R$.

The equation for a change in the mass of the ammonia M_{am} absorbed in a drop of radius R has the form

$$\frac{dM_{am}}{dt} = 4\pi R^2 \gamma_{am}\,(\mathrm{Re})\left(\rho_{am} - \rho_{eq}\,(M, R, T_d)\right). \tag{7}$$

The mass transfer coefficient of ammonia γ_{am} is defined by the expression $\gamma_{am}(\mathrm{Re}) = D_{am}(2 + 0.5\mathrm{Re}^{0.5})/2R$. The value of the coefficient of ammonia diffusion in air D_{am} was calculated by the Fuller method [4].

Using Henry's law [5] and the empirical values of Henry's constant H, which is dependent on temperature [6], we determine the equilibrium density of ammonia vapors ρ_{eq} over a drop of radius R that absorbed M_{am} of ammonia:

$$\rho_{eq}\,(M_{am}, T_d, R) \cong \frac{306}{\left(\dfrac{M_{am}}{17} + \dfrac{4\pi R^3 \rho_w}{3 \cdot 18}\right)}\,\frac{1\ \text{a.m.u.} \cdot M_{am} \cdot 10^5}{\mathrm{H}\,(T_d)\,kT_d}.$$

We note that with change in the temperature of the droplet from 20 to 0°C Henry's constant becomes twice as high. Thus, the evaporative cooling of a falling drop dependent on the moisture content of the air medium increases the absorptivity of water drops. It follows from Eq. (7) that as the concentration of ammonia in the drop increases, other conditions being equal, the rate of its absorption by the drop from the gas phase decreases. It is important to emphasize that if the ammonia density in the gas phase is close to an equilibrium, the dynamics of absorption starts to depend substantially on cooling of the drops.

The mathematical model (1)–(7) is a nonlinear system of ordinary differential equations with variable coefficients. The initial conditions ($t = 0$) have the form

$$x = x_0,\quad z = z_0,\quad v_x = v_{x0},\quad v_z = v_{z0};\quad R = R_0,\quad T_d = T_{d0},\quad M = 0. \tag{8}$$

Qualitative Estimates of the Absorption of Ammonia by Water Drops. Approximate analytical integration of Eq. (7) yields the following estimate for the mass of ammonia absorbed by a drop in the time of its fall t^*:

$$M_{am}\,(t^*) \sim \frac{\rho_{am}}{p_1}\left(1 - \exp\left(-D_{am}\,(2 + 0.5\mathrm{Re}^{0.5})\,2\pi R p_1 t^*\right)\right),\quad p_1 = \frac{3}{4\pi R^3}\,\frac{18\ \text{a.m.u.} \cdot 10^5}{\rho_w \mathrm{H}\,(T_d)\,kT_d}. \tag{9}$$

As follows from Eqs. (9), the mass of absorbed ammonia is directly proportional to the mass density of ammonia in air, whereas its dependence on the radius and time of fall of the drop is more complex. After series expansion in powers of exponent in Eq. (9) for small times of fall we obtain an approximate expression for the mass of ammonia:
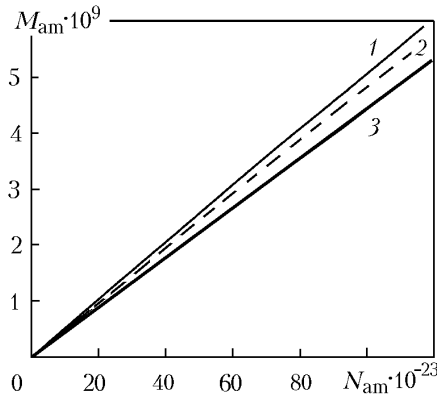
Fig. 2. Mass of ammonia absorbed by a drop in fall time t^*: 1) $R = 2.2$ mm; 2) 2.12; 3) 2.02 (total flow rate of mixture 117 liters/h, number density of ammonia before mixing of two streams 10^{23} molecules/m^3). M_{am}, kg; N_{am}, molecules/m^3.

$$M_{am} \sim p_1 D_{am} (2 + 0.5 \, \mathrm{Re}^{0.5}) \, R t^* \pi .$$ (10)

We note that the drop radius substantially influences the mass of absorbed ammonia.

Uniform distribution of ammonia (of the products of its decomposition) inside a water drop used for simplicity in our mathematical model is not attained instantly. However, in a large enough drop convective flows appear that favor the equalization of the concentration of ammonium and of the products of its interaction with water inside a drop [3] (a drop is considered large if its diameter exceeds 1 mm).

At the prescribed density of ammonia vapor its maximum mass in a drop M_{max} is easily determined from the right-hand side of Eq. (7) and Henry's law. The expression for M_{max} has the form

$$M_{max} = 10^{-5} \frac{4\pi R^3 \rho_w}{3} \frac{\rho_{am} H (T_d) k T_d}{18 \text{ a.m.u.}} .$$ (11)

In particular, for Henry's constant given above and for a drop of radius 2 mm at a temperature of 20°C and number density of ammonia in the gas phase of 1024 molecules/m^3 the value $M_{max} = 26.4 \cdot 10^{-7}$ kg and it is directly proportional to the ammonia density in a gas medium. The results of calculations show that during the experiment in the laboratory setup drops absorb a substantially smaller amount of ammonia in comparison with the maximum mass calculated by Eq. (11).

It is interesting to note that according to tabulated data [7] on the solvability of ammonia in water the maximum mass of ammonia in a drop of radius $R = 2$ mm can be equal to $2 \cdot 10^{-5}$ kg. Correspondingly, the molar fraction of ammonia is equal here to 0.39, the equilibrium numerical density of saturated vapors of ammonia at 27°C equals $2.9 \cdot 10^{26}$ molecules/m^3, and the mass density is equal to 8.24 kg/m^3. On dissolution of one mole of NH_3 in water 8.4 kcal is released [8, 9].

Numerical Results. The flow of a gas mixture in the experimental setup is laminar, since the Reynolds number calculated for the channel parameters and total flow rate of the mixture does not exceed 180. The calculations take into account changes in both the density and viscosity of the gas mixture, with the ratio of the flow rates of two streams in the setup being varied.

A substantial role in modeling absorption of ammonia by water droplets is played by the initial number density of ammonia molecules after the two streams have been mixed. In the gas mixture it was calculated in the approximation of instantaneous mixing.

The results of calculations of ammonia absorption for three values of drop radius and an initial number density of ammonia of 10^{23} molecules/m^3 in an ammonia-air flow corresponding to isothermal experimental conditions are given in Fig. 2. An increase in the flow rate of this initial flow, with the total flow rate of the gas mixture being pre-
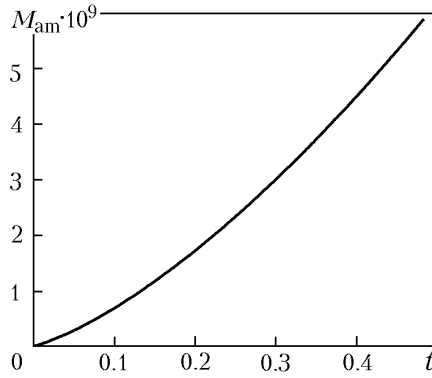
Fig. 3. Dynamics of the absorption of ammonia by a falling water drop. The values of parameters are same as in Fig. 2. M_{am}, kg; t, sec.

served, leads to an increase in the number density of ammonia in the gas mixture after mixing. It is seen that on increase in the ammonia flow rate, with the condition of total flow rate of the gas mixture being preserved, the mass of absorbed ammonia in a drop increases monotonically. Moreover, for drops of large radius the absorption rate is higher. This is mainly due to the increase in the product $R^2\gamma_{am}(\text{Re})$ (Eq. (7)). The equilibrium value of the ammonia density over a drop ρ_{eq} calculated with the aid of the Henry equation is an order of magnitude smaller than the corresponding value in the gas phase. Therefore, the release of gaseous ammonia from a drop during its fall can be neglected (the time of the drop fall is equal to about 0.5 sec). In modeling a laboratory experiment, evaporative cooling of drop can also be neglected.

FIgure 3 depicts the dynamics of absorption of ammonia by a falling water drop. An increase in the Reynolds number (in the drop velocity) leads to an increase in the rate of ammonia absorption. We call attention to the fact that most of the ammonia is absorbed at the end of drop fall, i.e., in the lower part of the experimental setup. A conclusion can be drawn that thorough mixing of the streams of air and ammonia at the inlet to the setup is important to obtain correct experimental results. Analytical estimation shows that for a channel with a diameter of 30 mm purely molecular mixing [6] will take the time

$$\tau \approx \frac{d^2}{\pi^2 D_{am}}, \tag{12}$$

which for our setup is $\tau \sim 9$ sec. Thus, in the case of a laminar flow and "poor" initial mixing of flow the concentration of ammonia in the channel equalizes due to molecular diffusion in the time needed for a drop to cover a distance equal approximately to one-third the length of the experimental setup.

As follows from Eq. (7), the content of ammonia in a drop is directly proportional to its concentration in the gas medium, which was directly confirmed in numerical calculations. It should be noted that in Fig. 3 the final molar concentration of ammonia in a drop is equal to $1.4 \cdot 10^{-4}$. This completely justifies our assumptions on the weak concentration of ammonia in the drop.

Following [3], it is not difficult to generalize the numerical results obtained for one drop to an ensemble of drops of one size. Let an ensemble of particles fall through a unit area rather than a single drop, so that the mass flow rate of water Q_w can be presented as

$$Q_w = 4\pi R^3 \rho_w N v/3 .$$

If we neglect the processes of disintegration and coalescence of drops, then the law of conservation of the number of drops, i.e., $Nv = N_0 v_0$, will hold. Then, as follows from Eq. (7), the mass of absorbate Γ contained in the drops of the ensemble is approximately equal to
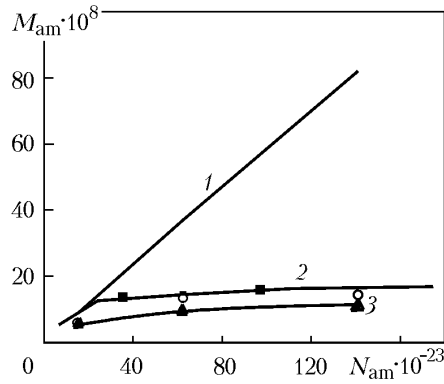
Fig. 4. Mass of ammonia in a drop depending on its number density in the gas phase: 1) numerical calculation; 2) experiment with a total flow rate of mixture of 170 liters/h; 3) experiment with a total flow rate of mixture of 80 liters/h; M_{am}, kg; N_{am}, molecules/m^3.
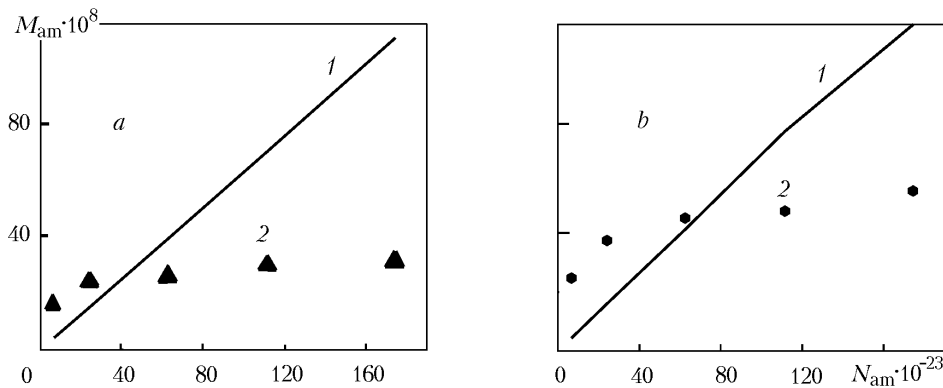

Fig. 5. Mass of ammonia in a drop with a total flow rate of a mixture of 117 liters/h depending on the number density of ammonia in the gas phase (a and b are masses of drops equal to 0.040 and 0.044 g): 1) numerical calculation; 2) experiment. M_{am}, kg; N_{am}, molecules/m^3.

$$\Gamma \sim \frac{Q_w}{Rv} \gamma_{am}.$$

This expression shows an increase in the absorption of ammonia on increase in the flow rate of water. At a fixed value of Q_w absorption increases with decrease in the radius of drops and their velocity. These conclusions agree completely with the results obtained in [2]. The change in the rate of absorption is related to the relative velocity of drops and gas flow via the mass transfer coefficient γ_{am}.

Comparison with Experiment. Figures 4 and 5 present dependences of the mass of ammonia in different sized drops on its number density N_{am} in the gas phase after mixing of streams. Both experimental and theoretical results are presented. It is seen that at low numerical densities of ammonia in a gas phase (to about $N_{am} = 3 \cdot 10^{24}$) and correspondingly at small masses of ammonia absorbed in a drop a good agreement between the predicted and experimental results was obtained.

The dependences of the mass of ammonia in a drop on its number density that were obtained at different total flow rates of the gas mixture are given in Fig. 4. Minimal experimental values are observed at the least total flow rate (curve 3). At the same predicted number density an appreciable increase in the mass of ammonia in a drop is observed on increase in the total flow rate of the mixture. Undoubtedly, this is due to the better mixing of the flows of air and ammonia at large gas-flow Reynolds numbers [10] for which the mathematical model gives a more reliable description

for experimental conditions. At high densities of ammonia in a gas mixture a substantial discrepancy is observed between the predicted and experimental data. While in the mathematical model the mass of ammonia in a drop is increased almost linearly with the law of increase in the number density of ammonia in a gas phase, in an experiment it virtually attains a constant value which increases noticeably with the drop radius. In particular, at the numerical density of ammonia $N_{am} = 18 \cdot 10^{24}$ the discrepancy attains 500% (Fig. 4). We note that on an inconsiderable increase in the radius of drops (approximately by 5-10%) the discrepancy decreases to 340-200% (Fig. 5) (in our experiments an equilibrium value of the content of ammonia in a water drop was not attained in the time the drop falls).

In order to correctly compare predicted and experimental data the high volatility of ammonia should be taken into account. Actually in the course of the experiment its volatility decreases the mass of the ammonia absorbed by water in the collecting beaker (the time needed to fill the beaker is inversely proportional to the cube of the radius of drops). In particular, at the numerical density of In particular, for the experiments shown respectively in Fig. 5a and b the time of filling the collecting beaker is 14 and 23% shorter than in the experiments presented in Fig. 4. The process of a decrease in the mass of ammonia in a collecting beaker cannot be described by our mathematical model. On the basis of Henry's law it can be shown that this process depends exponentially on the time of collection and number density of ammonia in the vicinity of the collecting beaker. In experiments the latter parameter is variable and does not exceed the value $N_{am} = 3 \cdot 10^{24}$. Using the obvious generalization of Eq. (7), we may approximately write the mass of ammonia $\overline{M}_{am}$ in a collecting beaker as a function of the time of the experiment t:

$$\overline{M}_{am}(t) = A \left[1 - \exp\left(-t/\tau\right)\right] . \tag{13}$$

From this it follows that if the time of an experiment is close to τ, then even small changes in the time needed to fill a collecting beaker can lead to substantial change in the absorbate mass.

Conclusions. The calculations have shown that the mass of ammonia absorbed by a single drop is directly proportional to the number density of ammonia in a gas phase: the larger the drop radius, the larger the mass of ammonia absorbed, which is due to the increase in the drop radius and in the mass-transfer coefficient. The slow chemical method of determining the mass of ammonia in a collecting beaker substantially underestimates the actual effectiveness of absorption.

More complex trajectories of the fall of drops lead to the necessity of allowing for their evaporative cooling [3]. Thus, there arises an interesting class of problems with important technical and ecological applications. In particular, to raise the effectiveness of absorption it is worthwhile to use aqueous solutions (note work [11] devoted to this problem).

NOTATION

A, theoretical weighted mean mass of absorbed ammonia in a collecting beaker on completion of experiment, kg; c, specific heat of water, J/(kg·K); C_d(Re), resistance coefficient; d, channel diameter, m; D_{am}, coefficient of diffusion of ammonia in air, m²/sec; D_w, coefficient of diffusion of steam in air, m²/sec; g, free fall acceleration, m/sec²; k, Boltzmann constant, J/K; m, mass of a spherical water drop, kg; M_{am}, mass of ammonia in a water drop, kg; $\overline{M}_{am}$, weighted mean mass of absorbed ammonia in a collecting beaker, kg; N, number of water drops passing through a unit area per unit time; N_{am}, number density of ammonia, molecules/m³; Q_w, mass flow rate of water, kg·m/sec; R, radius of a drop, m; Re, Reynolds number; t^*, time of drop fall, sec; t, time taken by experiment, sec; T, air temperature, K; T_d, temperature of a drop, K; u, velocity of ascending gas flow, m/sec; U, specific latent heat of phase transition of water, J/kg; U_{am}, specific heat of dissolution of ammonia in water, J/kg; $v = |\mathbf{v}| = (v_x^2 + (v_z - u)^2)^{0.5}$, rate of fall of a drop, m/sec; v_x, v_y, v_z, components of water drop rate vector in the Cartesian coordinate system, m/sec; x, y, z, axes of the Cartesian coordinate system, m; α(Re), coefficient of heat transfer of a drop, W/(m²·K); γ(Re), coefficient of mass transfer, m²/sec; Γ, mass of ammonia absorbed by water drops, kg; λ, thermal conductivity of a mixture, W/(m·K); μ, dynamic viscosity of air, kg/(m·sec); ρ, density of steam in air, kg/m³; ρ_{am},

density of ammonia in air, kg/m^3; ρ_{eq}, equilibrium density of ammonia vapor near the drop surface, kg/m^3; ρ_s, density of saturated steam, kg/m^3; ρ_w, density of water, kg/m^3; τ, characteristic time of concentration equalization, sec. Subscripts: 0, value at the initial moment; eq, equilibrium value; am, ammonia; d, drop; max, maximum; s, saturated steam; w, water.

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