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Model of aqueous salt solution droplet evaporation before the start of crystallization

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The paper proposes an approximate method for calculating the size and temperature of spherical droplets of aqueous salt solution (NaCl), which is applicable prior to the start of salt crystallization. The calculation results are in agreement with the results obtained via a more accurate model.

Keywords: evaporation, droplet, salt solution.

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Evaporation of liquid droplets has been investigated during many years. However, it turned out that this problem can hardly be solved completely and accurately [1]. At the same time, investigation of the evaporation process is important for a number of vital engineering applications [2,3]; thus, it would be convenient to have an approximate solution providing reliable estimates of the most important parameters of the process. Evaporation of a water droplet with salt dissolved in it is of interest, for instance, in connection with using sea water in creating mist curtains protecting offshore oil rigs against thermal radiation of a possible fire [4,5], in developing methods for sea water desalination [6], and also in various tasks of energetics, chemical technologies, biology and medicine [7–9].

As shown by the results of experiments [10] and calculations [11] on evaporation of pure water droplets, three stages of droplet evaporation can be distinguished: first, the droplet temperature quickly decreases due to heat loss for evaporation, then remains almost unchanged under temporary equilibrium between the convective heat supply and its consumption for evaporation, and, finally, evaporation causes a significant decrease in the droplet size. Typically, the longest time is taken by the second stage of the process. What is interesting is that similar temperature variations are also observed in fabricating thin membranes from polymer solutions [12]. While a droplet of aqueous salt solution evaporates, its concentration increases and evaporation rate decreases, after which the salt crystallizes with formation of a porous crust on the droplet surface [13–15]. The goal of this study was to construct an approximate model for estimating the solution droplet evaporation time and parameters up to the onset of salt crystallization.

Let us consider a spherical water droplet with initial radius R_0 and tablesalt mass concentration $C_{s,0}$. In many

of the above-mentioned applied problems, small droplets are flown around by moist air with constant pressure p_∞ , temperature T_∞ and relative humidity φ_∞ ; the flow Reynolds number calculated from the droplet diameter and speed relative to the air is less than unity. In this flow mode referred to as Stokes flow, the convective heat flow to the droplet is characterized by Nusselt number $Nu = 2$. The problem schematic diagram is presented in Fig. 1. The initial droplet temperature equals the air temperature, the droplet mass is

$$M_0 = (\rho_s C_{s,0} + \rho_w (1 - C_{s,0})) V_0,$$

where $V_0 = 4\pi R_0^3/3$ is the droplet volume, ρ_s, ρ_w is the salt density in water. The salt mass is $m_s = M_0 C_{s,0}$, the initial water mass in the droplet is $m_{0,w} = M_0 (1 - C_{s,0})$. Droplet temperature T may be obtained from heat balance equation

$$Mc \frac{dT}{dt} = 4\pi R [k(T_\infty - T) - RL\dot{m}], \quad T(0) = T_\infty, \quad (1)$$

where M is the mass of a droplet with radius R ; c is the solution specific heat per unit mass; k is the moist air thermal conductivity; \dot{m} is the mass flow of substance

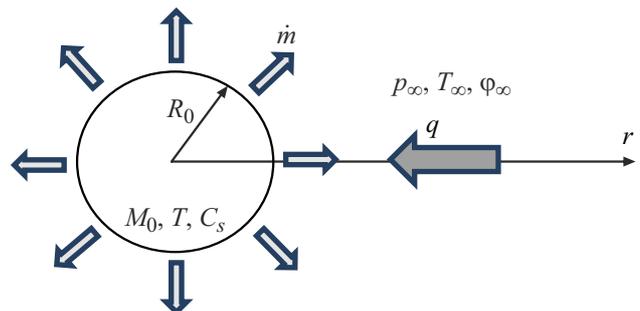


Figure 1. Schematic diagram of the problem.

Estimation of the approximate model accuracy

$C_{s,0}, \%$	R_*, mm	Approximate model					Complete model of evaporation				
		t_1, s	$T_1, ^\circ\text{C}$	$C_{s,1}, \%$	R_1, mm	t_*, s	t_1, s	$T_1, ^\circ\text{C}$	$C_{s,1}, \%$	R_1, mm	t_*, s
10	0.67	13.3	15.8	10.2	0.99	2023	128	15.4	10.7	0.98	1984
20	0.88	14.2	15.8	20.4	0.99	781	126	15.8	21.1	0.98	792
25	0.97	14.7	15.8	25.5	0.99	171	122	16.0	26.3	0.98	183

being removed from the droplet surface; L is the specific vaporization heat. The terms on the right side of the heat balance equation are the convective heat flow to the small droplet and heat removed from the droplet by evaporation. Numerical solution to the Cauchy problem (1) may be obtained using any standard program code.

The first stage of evaporation gets completed at $dT/dt = 0$ when the temperature stops decreasing and temporary equilibrium gets established between the convective heat input and evaporative heat removal: $k(T_\infty - T) = RL\dot{m}$. Since the substance is removed from the droplet surface due to diffusion, the following relation [11,16] is valid:

$$\dot{m} = -\frac{Dp_\infty}{RR_{gas}T_\infty} \ln \left[\frac{1 - (1-y)\frac{p_{sat}(T)}{p_\infty} \frac{\mu_w}{\mu_{gas}}}{1 - \varphi_\infty \frac{p_{sat}(T_\infty)}{p_\infty} \frac{\mu_w}{\mu_{gas}}} \right], \quad (2)$$

where D is the diffusion coefficient, R_{gas} is the moist air gas constant, μ_w and μ_{gas} are molar masses of water and moist air, $p_{sat}(T)$ is the saturated water vapor pressure at temperature T . According to the Raoult's law, term $(1-y)p_{sat}(T_s)$ in (2) accounts for variations in the saturated water vapor pressure which are caused by the presence of salt [17]. The salt mole fraction is defined as $y = (m_s/\mu_s)/[(m_s/\mu_s) + (m_w/\mu_w)]$. Since the logarithm value is low, formula (2) may be approximately presented in a simpler form:

$$\dot{m} = \frac{D}{RR_{gas}T_\infty} \frac{\mu_w}{\mu_{gas}} ((1-y)p_{sat}(T) - \varphi_\infty p_{sat}(T_\infty)). \quad (3)$$

At the first stage of evaporation, variations in the salt mass concentration are insignificant, and droplet temperature at the end of this stage T_1 may be estimated from relation

$$\frac{k}{L}(T_\infty - T_1) = \frac{D}{R_w T_\infty} ((1-y_0)p_{sat}(T_1) - \varphi_\infty p_{sat}(T_\infty)). \quad (4)$$

Here it is taken into account that $R_{gas}\mu_{gas} = \mathcal{R}$; \mathcal{R} is the universal gas constant; $R_w = \mathcal{R}/\mu_w$, y_0 is the salt molar fraction at the initial time moment. To estimate the first stage duration t_1 , let us use equation (1) and temperature T_1 from expression (4). Since the heat supply to the droplet is insignificant and evaporative mass flow is maximal, t_1 obeys the following relation:

$$\frac{T_1 - T_\infty}{t_1} = -\frac{4\pi RD}{R_w T_\infty} \frac{L}{Mc} p_{sat}(T_\infty)(1-y-\varphi_\infty). \quad (5)$$

Since the diffusion flux gradually decreases while heat supply to the droplet increases, the obtained estimate of t_1 is minimal.

The droplet radius variation with time will be determined by solving the following Cauchy problem:

$$\frac{dR}{dt} = -\frac{\dot{m}}{\rho_w}, \quad R(0) = R_0. \quad (6)$$

To assess the possibility that salt begins crystallizing before the completion of the first stage of the process, let us estimate the maximum possible variation in the droplet radius during the relevant time interval. Assuming that the droplet temperature remains T_∞ during time interval t_1 and the salt mass fraction is insignificant, obtain

$$\frac{R_1^2}{R_0^2} = 1 - \frac{2Dp_{sat}(T_\infty)}{\rho_w R_w T_\infty R_0^2} (1-\varphi_\infty)t_1. \quad (7)$$

The droplet mass and salt concentration at the end of the first stage are $M_1 = M_0 - \rho_w \Delta V$ and $C_{s,1} = m_s/M_1$ (here $\Delta V = V_0 - \frac{4}{3}\pi R_1^3$). As shown in [18], crystallization begins when the salt concentration in the solution reaches $C_s^* = 0.268$.

After the droplet has cooled to T_1 , all the heat supplied to it is spent on evaporation, and the droplet temperature remains unchanged. Therefore, the crystallization onset point t_* and respective droplet radius R_* are interrelated as follows:

$$R_*^2 = R_1^2 - \frac{2k}{\rho_w L} (T_\infty - T_1)(t_* - t_1). \quad (8)$$

To estimate the accuracy of the proposed approximate model, consider the case of droplet evaporation at $R_0 = 1 \text{ mm}$, $T_\infty = 27.5^\circ\text{C}$, and $\varphi_\infty = 27\%$; the initial salt mass concentration was varied from 10 to 25%. The Table and Fig. 2 present the results of comparing the estimates with calculations via the evaporation model [11] whose accuracy has been confirmed by experimental data [10]. Open diamonds and triangles in Fig. 2 indicate data obtained by using the simplified model. As expected, the approximate model significantly underestimates the duration of the first evaporation stage. At the same time, calculations of the crystallization onset time differ by no more than 7%. What is practically important is that a much simpler model provides correct estimates of the time point of the salt crystallization onset and of the droplet parameters at this time point.

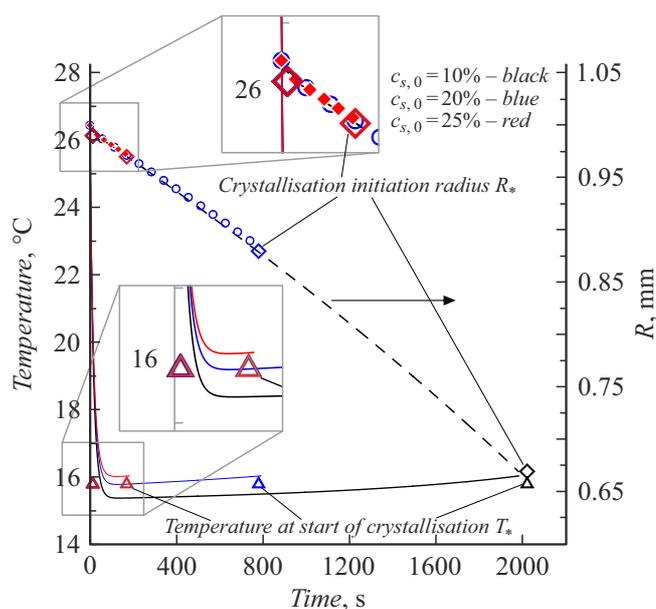


Figure 2. Results of calculations via the evaporation model given in [11] (lines, blue circles, red filled diamonds) and via the simplified model (open diamonds and triangles) for $R_0 = 1$ mm, $T_\infty = 27.5^\circ\text{C}$, $\varphi_\infty = 27\%$, and various initial mass concentrations of salt. The colored figure is given in the electronic version of the paper.

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Conflict of interests

The authors declare that they have no conflict of interests.

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