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## Abstract

## Full Text

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# Kinetics of Distillation in a Supercooled System

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1. In supercooled systems, when droplets, crystals, and vapor are simultaneously present over a considerable temperature interval, distillation is the principal process determining the change in the state of the system with time. It leads to continuous growth of the crystals, evaporation of the droplets, and gradual change in the vapor density. Usually this phenomenon is complicated by a number of circumstances; however, the analysis of the question carried out in ([1]) shows that the simplest scheme considered below is the fundamental one.

The purpose of the present work is to investigate the kinetics of distillation in pure form and to construct a simple scheme for calculating the phenomenon in any particular case.

2. Let us introduce the notation: $a = a(t)$ is the radius of a particle, $\rho$ is the density of the substance of the particle; $n$ is the number of particles per unit volume, with subscript 1 referring to droplets and subscript 2 to crystals; $D$ is the diffusion coefficient of vapor in air; $c = c(t)$ is the vapor density, where $c_1$ corresponds to saturation of the vapor over droplets, and $c_2$ over crystals,

$$\Delta c = c_1 - c_2 > 0. \tag{1}$$

Assuming that at the initial instant $t = 0$ the system consists of supercooled droplets, crystal nuclei whose radius $a_1(0)$ is negligibly small, and vapor whose density corresponds to saturation over a supercooled droplet, the initial conditions of the process will be

$$a_1(0), \quad a_2(0) = 0, \quad c(0) = c_1. \tag{2}$$

The transfer process is described by the system of differential equations

$$\frac{dc}{dt} = 4\pi n_1 a_1 D(c_1 - c) + 4\pi n_2 D(c_2 - c)a_2, \tag{3}$$

$$\rho_1 a_1 \frac{da_1}{dt} = D(c - c_1), \tag{4}$$

$$\rho_2 a_2 \frac{da_2}{dt} = D(c - c_2). \tag{5}$$

The system (3)–(5), with the initial conditions (2), constitutes a Cauchy problem. From (3)–(5) we immediately obtain two integrals

$$c(t) + {}^4\!/_3 \pi \rho_1 n_1 a_1^3(t) + {}^4\!/_3 \pi \rho_2 n_2 a_2^3(t) = M, \tag{6}$$

$$\rho_1 a_1^2(t) - \rho_2 a_2^2(t) = \rho_1 a_1^2(0) - 2D\Delta c\, t. \tag{7}$$

With the aid of (6) and the change of variables

$$X = \sqrt[3]{\left({}^4\!/_3 \pi \frac{n_2 \rho_2}{M - c_2}\right)^2 a_2^2(t)}, \tag{8}$$

$$Y = \frac{\Delta}{a_1^2(0)} a_1^2(t) \tag{9}$$

equations (4) and (5) can be reduced to a single differential equation (for details see ([2]))

$$\frac{dY}{dX} = \left(\frac{\rho_2}{\rho_1}\right)^{1/3} \nu^{-2/3} \frac{X^{3/2} + Y^{3/2} - \Delta^{3/2}}{X^{3/2} + Y^{3/2} - 1}, \qquad Y(0) = \Delta. \tag{10}$$

Here

$$\nu = n_2/n_1, \tag{11}$$

$$\Delta = \frac{q_1(0)}{\Delta c + q_1(0)}, \qquad q_1(0) = \frac{4}{3}\pi \rho_1 n_1 a_1^3(0). \tag{12}$$

Let the time during which the entire distillation process takes place be denoted by $T^*$. We shall determine it from the condition that the process is completely finished when the vapor density $c(t)$ reaches the value $c_2$, i.e.,

$$c(T^*) = c_2. \tag{13}$$

By virtue of the uniqueness of the solution of the Cauchy problem (2)–(5), (13) uniquely determines $T^*$, $a_1(T^*)$, and $a_2(T^*)$.

3. A rigorous analysis of the problem was carried out in ([2]). We note the following conclusions.

1) The process is divided into two stages. The time of the first stage $T$ corresponds to complete evaporation of the droplets, i.e. $a_1(T) = 0$. In this case

$$a_2(T) = \sqrt{X_I}\, a_{2\max}, \tag{14}$$

where

$$\Delta < X_I < 1, \tag{15}$$

$a_{2\max}$ is the maximum possible radius of the crystal,

$$a_{2\max} = \sqrt[3]{\frac{M - c^2}{\frac{4}{3}\pi\rho_2 n_2}}. \tag{16}$$

The time $T$ is determined by the formula

$$T = \frac{\rho_2 a_{2\max}^2 X_I + \rho_1 a_1^2(0)}{2D\Delta c}. \tag{17}$$

2) The second stage of the process, during which $a_1 = 0$, consists in the condensation of the excess amount of vapor on the crystals. It lasts infinitely long owing to the asymptotic approach of $dc/dt$ to zero. Practically, it is expedient, for example, to assume that the second stage continues for a time $T'$, during which the crystal reaches not less than 96% of its maximum value. Then

$$T' = \frac{1}{\pi n_2 D a_{2\max}}, \tag{18}$$

and the total time of the process is

$$T^* \simeq \frac{\rho_2 a_{2\max}^2 X_I + \rho_1 a_1^2(0)}{2D\Delta c} + \frac{1}{\pi n_2 D a_{2\max}}. \tag{19}$$

3) We shall estimate the role of each stage by the relative increase in the radii of the crystals. The formulas are

$$a_{2\mathrm{I}} = \sqrt{X_I}\, a_{2\max}, \qquad a_{2\mathrm{II}} = \left(1 - \sqrt{X_I}\right) a_{2\max}, \qquad \Delta < X_I < 1, \tag{20}$$

where $a_{2\mathrm{I}} = a_2(T)$ and $a_{2\mathrm{II}}$ are the increments of the radii during the first and second stages. We note that for $X_I > 0.9$ the second stage can, to an accuracy of 5%, be neglected altogether.

4) $X_1$ is determined, for the given substance, by $\Delta$ and $\nu$, and $X_1$ decreases both with decreasing $\Delta$ and with decreasing $\nu$. The decrease in $\Delta$ is caused by an increase in $\Delta c^*$—the fraction of the substance in the vapor state, distilled into the crystals, relative to the fraction of the substance in the liquid state, $q_1(0) = \frac{4}{3}\pi n_1 \rho_1 a_1^3(0)$. The decrease in $\nu$ at fixed $\Delta$, $\Delta c$, and $a_1(0)$ occurs owing to a decrease in $n_2$—the number of crystal nuclei.

Let us note that, independently of $\Delta$, for $n_2 \ll n_1$, i.e., for $\nu \ll 1$, the quantities $a_{2\mathrm{I}}$, $a_{2\mathrm{II}}$, and $a_{2\,\max}$ are of order $\nu^{-1/3}$.

5) The value of $X_1$ can be determined directly from $\Delta$ and $\nu$ (for more detail see item 4), i.e., directly from the input data, without first calculating the kinetics of the first stage of the process. Thus, by formulas (17), (19), and (20), the time of the first stage, the time of the entire process, and also the increments of the crystal radii $a_{2\mathrm{I}}$ and $a_{2\mathrm{II}}$ are immediately determined.

4. To calculate the kinetics of the first stage it is necessary to solve numerically the differential equation (10), which depends on two parameters $\Delta$ and $\nu$**. To simplify this cumbersome operation, we have compiled a set of solutions of equation (10) corresponding to a broad range of values of $\Delta$ and $\nu$: $\Delta = 0.1(0.1)0.9$; $\nu = 10^{-3}$; $10^{-2}$; $10^{-1}$; 0.2; 0.5; 1; 2.5; 10; $10^2$; $10^6$. These solutions are presented in the form of tables of the special function $Y = F(X; \Delta; \nu)$ for $X$ in the interval $(0, 1)$ with $\Delta X = 0.05$ (or 0.1) (see (2), Tables 1-9). In addition, in (2) Table 10 is given for determining $X_1$ from $\Delta$ and $\nu$. When using the tables in (2), one should take into account the "correction for the substance." The point is that the tables were compiled as applied to water. Therefore, in order to use Tables 1-10 in analyzing the distillation of another substance, as the input parameter in the tables $\nu$ one should take not $n_2/n_1$, but the quantity $\nu'$,

$$\nu' = \sqrt{\frac{1.9\sigma_1}{\rho^2}}\,\nu. \tag{21}$$

The calculation is performed as follows. With the aid of Tables 1-9 (2), for the given $\Delta$ and $\nu'$, we find from $X$ the corresponding values of $Y$. Using (8) and (9), from $X$ and $Y$ we pass to $a_2(t)$ and $a_1(t)$. Taking into account

$$M = c_1 + q_1(0), \tag{22}$$

from (6) we find $c(t)$. The time $t$ corresponding to these $a_2(t)$, $a_1(t)$, and $c(t)$ is determined from (7).

5. In analyzing the second stage it is convenient to introduce into consideration the time

$$\tau = t - T, \tag{23}$$

measured from the end of the first stage. For $X_1$ satisfying the condition

$$0.65 \leqslant X_1 < 1, \tag{24}$$

the calculation of the kinetics of the second stage, with an error not exceeding 10%, may be carried out by the approximate formula

$$\alpha(\tau) = \alpha_0 e^{-\beta\tau}, \qquad 0 \leqslant \tau \leqslant T', \tag{25}$$

where

$$\alpha(\tau) = \frac{a_{2\max} - a_2(\tau)}{a_{2\max}}, \qquad \alpha_0 = 1 - \sqrt{X_1}. \tag{26}$$

$$\beta = 4\pi n_2 D a_{2\max}. \tag{27}$$

* $\Delta c$ depends on the temperature at which distillation takes place.

** $(\rho_2/\rho_1)^{1/3}$ may be included in $\nu$.

If condition (24) does not hold, then the calculation becomes somewhat more complicated (see (2)).

$c(\tau)$ in the second stage is determined by the formula

$$c(\tau) = M - \frac{4}{3}\pi\rho_2 n_2 a_2^3(\tau). \tag{28}$$

6. The scheme developed above contains a complete analysis of the problem posed and makes it possible to calculate rapidly the kinetics of both stages of the distillation process. Let us turn to some physicochemical conclusions.

1) Figure 1 gives curves describing the first stage of distillation in the vapor–water–ice system at $t = -20°$, $n_1 = 60$ cm$^{-3}$, $n_2 = 6$ cm$^{-3}$, $a_1(0) = 10\mu$. Along with the curves $a_1(t)$ and $a_2(t)$, Fig. 1 also gives the curve for the quantity $c^*(t)$,

$$c^*(t) = \frac{c_1 - c(t)}{\Delta c}, \tag{29}$$

characterizing the relative change in density during the first stage of distillation. It is interesting that, despite the fact that the water drops are 10 times larger than the crystals, by the end of the first stage of the process the vapor density

differs from $c_1$ by 36.5% (in fractions of $\Delta c$). The time of the first stage here is 83.9 sec., the value $X_1 = 0.809$. The second stage is described by the formula $\alpha(\tau) = 0.982\, e^{-0.040\tau}$. Its duration is $T' = 10$ sec., and the total distillation time $T^* \simeq 94$ sec.

**Fig. 1** **Fig. 2**

2) The relative change in vapor density by the moment of complete evaporation of the drops is

$$c^*(T) = \frac{M - c_2}{\Delta c}\sqrt{X_1^3} = \frac{q_1(0)}{\Delta c}, \qquad \Delta c = M - c_2 - q_1(0). \tag{30}$$

The dependence of $c^*(T)$ on the number of introduced crystal nuclei, $n_2$, for the example given above is shown in Fig. 2 ($c^*_\nu(T)$ in the graph). Note that in (30) only $X_1$ depends on $n_2$. From Fig. 2 it is seen that practically at $\nu < 0.01$, while the drops exist, the concentration is equal to $c_1$; at $\nu > 10$ by the moment of complete evaporation of the drops it becomes equal to $c_2$, and therefore there will be no second stage of distillation. Of interest is the almost linear course of $c^*$ as a function of $\lg \nu$ in the interval of $\nu$ from 0.01 to 10.

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## CITED LITERATURE

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*Note: Figure translations are in progress. See original paper for figures.*