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# PHYSICAL CHEMISTRY

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**Abstract**

**Full Text**

## PHYSICAL CHEMISTRY

M. V. BUIKOV

### ISOTHERMAL DISTILLATION IN THE SYSTEM

### WATER FOG—FOG OF A DILUTE SOLUTION

*(Presented by Academician A. N. Frumkin, December 20, 1960)*

In a number of problems connected with the study of mixtures of different fogs, the kinetics of distillation due to the difference in the concentrations of saturated water vapor over fog droplets of different components is of great importance. In particular, the question of the kinetics of distillation from water droplets onto ice crystals has been well studied<sup>(1-3)</sup>.

The subject of the present note is the study of distillation from water droplets onto droplets of a dilute solution. The system of equations describing the distillation process has the form

$$\begin{aligned}\rho_1 r_1 \frac{dr_1}{dt} &= D(u - u_1), \\ \rho_2 r_2 \frac{dr_2}{dt} &= D(u - u_2),\end{aligned}\tag{1}$$

$$\frac{du}{dt} + 4\pi D n_1 r_1 (u - u_1) + 4\pi D n_2 r_2 (u - u_2) = 0,$$

where the following notation has been introduced:  $r_1, \rho_1, n_1$  and  $r_2, \rho_2, n_2$  are the radii, densities, and concentrations, respectively, of droplets of pure water and of solution;  $u$  is the density of water vapor;  $u_1$  and  $u_2$  are the corresponding saturated densities of water vapor;  $D$  is the coefficient of diffusion of water vapor in air.

Substituting into (1) the value of  $u_2$  according to Raoult's law,

$$u_2 = u_1(1 + \gamma r_2^{-3}); \quad \gamma r_2^{-3} \ll 1; \quad \gamma = \frac{3m\mu_w}{4\pi\rho_1\mu_s}$$

(where  $m$  is the mass of dissolved substance in one solution droplet;  $\mu_w, \mu_s$  are the molecular weights of water and of the dissolved substance), introducing the new function  $u' = u - u_1$  and omitting the prime, we obtain

$$\begin{aligned}\rho_1 r_1 \frac{dr_1}{dt} &= Du, \\ \rho_2 r_2 \frac{dr_2}{dt} &= D(u + u_1 \gamma r_2^{-3}),\end{aligned}\quad (2)$$

$$\frac{du}{dt} + 4\pi D n_1 r_1 u + 4\pi D n_2 r_2 (u + u_1 \gamma r_2^{-3}) = 0.$$

Initial conditions:

$$r_1 = r_{10}, \quad r_2 = r_{20}, \quad u = 0 \quad \text{at } t = 0.$$

In solving system (2) we use the so-called “quasi-stationary” approximation<sup>(1,2)</sup>, which consists in the fact that the concentration of water-

of the vapor in the first approximation is regarded as constant. Setting  $du/dt \simeq 0$  in the third equation of (2), we find:

$$u = -u_1 \nu r_2^{-3} \left( 1 + \frac{n_1 r_1}{n_2 r_2} \right)^{-1}. \quad (3)$$

From (3) it is seen that the initial condition  $u = 0$  is approximately satisfied for dilute solutions. Differentiating (3) with respect to time, we obtain

$$\left| \frac{du}{dt} \frac{T}{u_1} \right| = \frac{u}{u_1} \left[ T \frac{dr_1}{dt} \frac{n_1}{n_1 r_1 + n_2 r_2} + T \frac{dr_2}{dt} \left( \frac{2}{r_2} + \frac{n_1}{n_1 r_1 + n_2 r_2} \right) \right], \quad (4)$$

where  $T$  is the time during which the droplets of water fog evaporate completely; it is the characteristic time of the problem. From (4) it follows that the condition for applicability of the adopted approximation,

$$\left| \frac{du}{dt} \frac{T}{u_1} \right| \ll 1,$$

is fulfilled, since  $u \ll u_1$ , while all terms in the square bracket have values of order unity.

In view of the fact that time does not enter explicitly into (2),  $r_2$  may be regarded as a function of  $r_1$ :  $r_2(r_1)$ . Taking this into account and using (3), it is not difficult to obtain

$$r_2^2 dr_2 = -\nu r_1^2 dr_1; \quad r_2 = r_{20} \text{ for } r_1 = r_{10}; \quad \nu = \frac{\rho_1 n_1}{\rho_2 n_2}. \quad (5)$$

Integrating (5) and using the initial condition, we obtain

$$r_2 = r_m (1 - \nu r_1^3 r_m^{-3})^{1/3}; \quad r_m = r_{20}(1 + \alpha)^{1/3}; \quad \alpha = \frac{n_1 \rho_1 r_{10}^3}{n_2 \rho_2 r_{20}^3}; \quad (6)$$

$r_m$  is the radius attained by the solution droplets at the moment when the water droplets disappear.

From the first equation of (2) we find:

$$\int_{r_{10}}^{r_1} \frac{r' dr'}{u(r')} = \frac{D}{\rho_1} t. \quad (7)$$

Using (3), (6), and (7), after simple calculations we obtain an implicit dependence  $r_1(t)$ :

$$t = t_0 J \left( \frac{r}{r_{10}} \right),$$

$$J(x) = \frac{1}{2}(1-x^2) \beta(1+\alpha)^{-2/3} - \frac{1}{5}(1-x^5) \alpha \beta(1+\alpha)^{-5/3} + \frac{\rho_2}{5\rho_1} \left( 1 - \frac{\alpha}{1+\alpha} x^3 \right)^{5/3} - \frac{\rho_2}{5\rho_1} (1+\alpha)^{-5/3}; \quad (8)$$

$$t_0 = \frac{r_m^3}{\gamma} \frac{\rho_1 r_m^3}{Du_1}; \quad \beta = \frac{r_{10}^2}{r_{20}^2}.$$

The time of complete evaporation of the droplets of water fog  $T$  is determined by the equation

$$T = t_0 J \left( \frac{r_1}{r_{10}} \right) \Big|_{r_1=0}. \quad (9)$$

As is seen from (8),  $J(x)$ , and also  $J(0)$ , depend on two parameters: the ratio of the water content to the mass of solution per unit volume  $\alpha$ , and the ratio of the surfaces of the water and solution droplets  $\beta$  at the initial instant of time. Depending on the magnitude of these parameters, a number of simple formulas can be obtained for the time of complete evaporation of the water droplets: for  $\alpha \gg 1$ , i.e., when the mass of the introduced solution is much less than the water content, and  $\beta \lesssim 1$ ,

$$T = \frac{r_{20}^3}{\gamma} \frac{\rho_2 r_{20}^2}{5Du_1} \alpha^{5/3}. \quad (10)$$

The same formula is valid for  $1 \ll \beta \ll \alpha^{2/3}$ . For  $1 \ll \alpha^{2/3} \ll \beta$  we have the formula

$$T = 0.3 \frac{r_{20}^3}{\gamma} \frac{\rho_1 r_{10}^2}{Du_1} \alpha. \quad (11)$$

It follows from (10) and (11) that, keeping  $\alpha$  and  $r_{10}$  constant and taking the solution in the form of smaller droplets, we can reduce  $T$ . In the opposite limiting case,  $\alpha \ll 1$  and  $\beta \gtrsim 1$ , we have

$$T = \frac{r_{20}^3}{\gamma} \frac{\rho_1 r_{10}^2}{2Du_1}. \quad (12)$$

The last formula is also valid for  $1 \gg \beta \gg \alpha$ . In the case  $1 \gg \alpha \gg \beta$ , we obtain

$$T = \frac{r_{20}^3}{\gamma} \frac{\rho_2 r_{20}^2}{3Du_1} \alpha, \quad (13)$$

and in this case a decrease in the initial radius of the solution droplets leads to a decrease in  $T$ . We note that formula (12) gives the evaporation time of a single water droplet placed among solution droplets.

Since the problem was solved for monodisperse fogs, whereas real fogs are polydisperse, it is of interest to consider distillation in a mixture of polydisperse fogs, which will be the subject of a separate communication.

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

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