SovietRxiv

Soviet-era science, translated into English

Corresponding Member of the Academy of Sciences of the USSR B. V. Deryagin, Yu. S. Kurgin

1964

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196401.18502

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR B. V. Deryagin, Yu. S. Kurgin

Nonstationary Evaporation of a Drop Covered by an Adsorption Layer

Previously we ([1]) considered the effect of monolayers on the evaporation of drops. We obtained the formula for the rate of evaporation of a drop through a monolayer by a limiting transition from a macroscopic film to a monolayer, considering the diffusion of the molecules of the drop liquid in the film. However, this method is not the only one, and here we shall give a more general derivation of the rate of evaporation of a drop through a monolayer. In addition, in ([1]), in the treatment of nonstationary evaporation of a drop through a monolayer, an inaccuracy was allowed in the boundary condition, which led to an error in the formula for the rate of nonstationary evaporation.

Let us consider the nonstationary evaporation of a liquid drop of radius a, covered by a monolayer of a foreign substance, stationary with respect to an infinitely extended gaseous medium. We choose the origin of coordinates at the center of the drop. Let, at the initial moment, the vapor concentration in space be constant and equal to

$$c(r, 0) = c_\infty. \tag{1}$$

On the surface of the monolayer of the foreign substance an adsorption layer of vapor is formed. Let us consider the establishment of adsorption equilibrium. We assume the adsorption, which we denote by Γ (molec/cm^2), to be small. Adsorption of vapor on the monolayer can proceed by two paths: from the liquid through the monolayer and from the vapor. Let the mean desorption time of vapor molecules into the liquid be equal to τ_1, and the mean desorption time into the vapor be equal to τ_2; then the adsorption fluxes into the liquid and into the vapor are respectively $\gamma_1\Gamma$ and $\gamma_2\Gamma$, where $\gamma_1 = 1/\tau_1$ and $\gamma_2 = 1/\tau_2$. If the flux of molecules of the drop liquid through the monolayer is denoted by J (for small Γ, J does not depend on Γ), then the resultant flux through the monolayer, taking desorption into account, is equal to $\Lambda = J - \gamma_1\Gamma$. In the vapor phase we take into account the transport of molecules without collisions over the mean free path.

For small Γ, the resultant flux into the vapor is equal to $\left[\gamma_2\Gamma - \alpha\frac{\bar{v}}{4}c\big|_{r=a+\lambda}\right]$, where α is the condensation coefficient, $\bar{v}$ is the mean velocity of vapor molecules

SovietRxiv

at the temperature of the drop. We write the mass-balance condition for the adsorption layer of vapor:

$$\left[(J-\gamma_1\Gamma)-\left(\gamma_2\Gamma-\alpha\frac{\bar{v}}{4}c\Big|_{r=a+\lambda}\right)\right]=d\Gamma/dt. \tag{2}$$

As a result of solving equation (2), we obtain the formula:

$$\Gamma=\Gamma_0 e^{-(\gamma_1+\gamma_2)t}+\left(J+\alpha\frac{\bar{v}}{4}c\Big|_{r=a+\lambda}\right)/(\gamma_1+\gamma_2)$$

(where Γ_0 is a certain constant), from which it is seen that the time for establishing adsorption equilibrium is $\tau=1/(\gamma_1+\gamma_2)=\tau_1\tau_2/(\tau_1+\tau_2)$ and is determined, mainly, by the smaller of the times of the separate processes: desorption into the liquid and desorption into the vapor. After the establishment of adsorption equilibrium

$$d\Gamma/dt=0, \tag{3}$$

and the magnitude of the adsorption flux into vapor $\gamma_2\Gamma$ we express from the following considerations. In the absence of a monolayer, the adsorption flux into vapor $\gamma_2\Gamma$ would be equal to the evaporation rate $\alpha\frac{\bar{v}}{4}c_S(T_0)$, where $c_S(T_0)$ is the concentration of saturated vapor at the drop temperature. We assume that the influence of the monolayer on evaporation can be reduced to a decrease in the effective concentration from which the vapor evaporates by an amount proportional to the resulting flux of molecules through the monolayer Λ, i.e., by $R\Lambda$, where the proportionality coefficient is denoted by R. Such a treatment presents a certain analogy with Ohm' s law. As a result we obtain the condition:

$$\Lambda-\left\{\alpha\frac{\bar{v}}{4}\left[c_S(T_0)-\Lambda R\right]-\alpha\frac{\bar{v}}{4}c\Big|_{r=a+\lambda}\right\}=0. \tag{4}$$

From the equality, at the boundary $r=a+\lambda$, of the molecular flux of vapor to the diffusion flux of vapor in the gas, we obtain the condition

$$4\pi a^2\alpha\frac{\bar{v}}{4}\left\{\left[c_S(T_0)-\Lambda R\right]-c\Big|_{r=a+\lambda}\right\}=4\pi(a+\lambda)^2\left(-D\frac{\partial c}{\partial r}\Big|_{r=a+\lambda}\right), \tag{5}$$

where D is the coefficient of diffusion of vapor in the gas. From formulas (4) and (5) we obtain the boundary condition:

SovietRxiv

$$\left.\frac{\partial c}{\partial r}\right|_{r=a+\lambda} = \frac{1}{a+\lambda}\left[\frac{1}{D}\frac{a^2}{a+\lambda}\Big/\left(R+\frac{1}{\alpha\bar{v}/4}\right)\right]\left[c\big|_{r=a+\lambda} - c_S(T_0)\right]. \qquad (6)$$

We solve the equation of nonstationary diffusion of vapor in air under condition (3):

$$D\Delta c = \partial c/\partial t, \qquad r > a+\lambda, \qquad t > 0, \qquad (7)$$

with conditions (1) and (6). Defining the evaporation rate as

$$I = -dM/dt = m \cdot 4\pi(a+\lambda)^2\left(-D\,\partial c/\partial r\big|_{r=a+\lambda}\right), \qquad (8)$$

where M is the mass of the drop, m is the mass of a vapor molecule, and substituting $\partial c/\partial r|_{r=a+\lambda}$ from the solution of equation (7), we obtain:

$$I = \frac{m \cdot 4\pi a^2[c_S(T_0) - c_\infty]}{R + 1/(\alpha\bar{v}/4) + (1/D)(a^2/(a+\lambda))}[1+f(t)], \qquad (9)$$

where

$$f(t) = \frac{(1/D)(a^2/(a+\lambda))}{R+1/(\alpha\bar{v}/4)}\left\{\exp\left[\frac{Dt}{(a+\lambda)^2}\left(\frac{R+1/(\alpha\bar{v}/4)+(1/D)(a^2/(a+\lambda))}{R+1/(\alpha\bar{v}/4)}\right)^2\right]\right\}\times$$

$$\times\left[1-\operatorname{erf}\left(\frac{\sqrt{Dt}}{a+\lambda}\frac{R+1/(\alpha\bar{v}/4)+(1/D)(a^2/(a+\lambda))}{R+1/(\alpha\bar{v}/4)}\right)\right].$$

For

$$t \gg T_0 = \frac{(a+\lambda)^2}{D}\left(\frac{R+1/(\alpha\bar{v}/4)}{R+1/(\alpha\bar{v}/4)+(1/D)(a^2/(a+\lambda))}\right)^2, \qquad f(t) \to 0,$$

the initial nonstationarity dissipates, and a quasi-stationary evaporation regime is established, whose rate is equal to

$$I_0 = \frac{m4\pi a^2[c_S(T_0) - c_\infty]}{R + 1/(\alpha\bar{v}/4) + (1/D)(a^2/(a+\lambda))}. \qquad (10)$$

From formula (10) it is seen that R can be interpreted as the resistance of the monolayer to evaporation; $1/(\alpha\bar{v}/4)$ is the resistance of incomplete "sticking"

SovietRxiv

of vapor molecules to the monolayer, and $(1/D)(a^2/(a+\lambda))$ is the diffusion-enabling

resistance. The time T_0 for

$$R + \frac{1}{\alpha\bar{v}/4} \gg \frac{1}{D}\frac{a^2}{a+\lambda}$$

is equal to $T_0 = (a+\lambda)^2/D$, and for

$$\frac{1}{D}\frac{a^2}{a+\lambda} \gg R + \frac{1}{\alpha\bar{v}/4}$$

is equal to

$$T_0 = D\left(R + 1/(\alpha\bar{v}/4)\right)^2 \cdot \frac{(a+\lambda)}{a^4}.$$

The rate of evaporation of the drop at the initial moment is

$$I\big|_{t=0} = \frac{m \cdot 4\pi a^2 \left[c_S(T_0) - c_\infty\right]}{R + 1/(\alpha\bar{v}/4)}. \tag{11}$$

Under the condition $R + 1/(\alpha\bar{v}/4) < 1/(\alpha_{\mathrm{H_2O}}\bar{v}/4)$, where $\alpha_{\mathrm{H_2O}}$ is the condensation coefficient of water, the monolayer in the initial period of evaporation must increase the evaporation rate of water, which agrees with experiment ([2]).

As a result of the analogous solution of the nonstationary problem with condition (3) for evaporation from a plane surface of a liquid covered by a monolayer, we obtain the expression for the evaporation rate from 1 cm^2 of surface:

$$I' = \frac{m\left[c_S(T_0) - C_L\right]}{R + 1/\left(\alpha\frac{\bar{v}}{4}\right)}\left\{\frac{1}{1+p} + 2p\sum_{n=1}^{\infty}\frac{\exp[-D\gamma_n^2 t/(L-\lambda)^2]}{\gamma_n^2 + p(p+1)}\right\},$$

where C_L is the vapor concentration in air at a distance L from the liquid surface, $(L-\lambda)$ is the thickness of the diffusion layer of air,

$$p = \frac{[(L-\lambda)/D]}{\left[R + 1/\left(\alpha\frac{\bar{v}}{4}\right)\right]},$$

γ_n are the roots of the transcendental equation

$$\operatorname{tg}\gamma_n = -\gamma_n/p.$$

SovietRxiv

For $t \gg (L-\lambda)^2/(D\gamma_1^2)$, a stationary evaporation regime is established, whose rate is equal to

$$I_0' = \frac{m\left[c_S(T_0) - C_L\right]}{(L-\lambda)/D + R + 1/\left(\alpha\frac{\bar{v}}{4}\right)},$$

and at the initial moment:

$$I'\big|_{t=0} = \frac{m\left[c_S(T_0) - C_L\right]}{\left[R + 1/\left(\alpha\frac{\bar{v}}{4}\right)\right]}.$$

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
2 I 1964

CITED LITERATURE

1. B. V. Deryagin, S. P. Bakanov, Yu. S. Kurgin, *DAN*, **135**, 1417 (1960).

2. M. V. Tovbin, E. V. Savinova, *ZhFKh*, **31**, 2717 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.