Capillary solution evaporation theory is presented, which incorporates crystal formation near the mouth when supersaturation is reached; high evaporation rates and high solution concentrations can result in a transient state, where the crystal size pulsates.

An aqueous solution evaporating from a capillary for \( p_0 < p_m \) produces a gradual increase in the nonvolatile-component concentration (e.g., salt) near the meniscus; the salt diffuses back into the capillary if the meniscus position is unchanged (by solution supply), and a stationary state occurs, with a certain constant value \( C_m > C_0 \) [1, 2].

At high evaporation rates, \( C_m \) may exceed \( C_s \), which leads to crystals being deposited, as observed for aqueous solutions of potassium dichromate in glass capillaries [3]. The crystals narrow the capillary, which reduces the evaporation rate and correspondingly the flow speed. However, a lower \( v \) corresponds to a smaller \( C_m \), which may become less than \( C_s \), so the crystal partly dissolves. A crystal volume reduction again increases the evaporation rate, so the concentration rises again near the meniscus, which may cause the crystal to grow. The transition to the stationary state may involve crystal volume oscillations.

The oscillating conditions may be established by considering the evaporation of an aqueous salt solution (Fig. 1); the meniscus is in a fixed position, which is provided, as in [3], by narrowing at the end and the liquid being drawn up to the mouth. The capillary communicates with the vessel maintaining a constant concentration \( C_0 \). The condition \( L \gg r_0 \) allows one to neglect edge effects.

Convection in the air near the mouth produces a diffusion layer, thickness \( \varepsilon \), within which the vapor pressure falls linearly from \( p_m \) to \( p_0 \) [4]. The evaporation rate is then defined by the diffusion equation

\[
\alpha = \frac{D_{0}v_{m}}{RT\delta} (p_m - p_0).
\]  

The concentration distribution \( C(x) \) along the capillary is found by solving the convective-diffusion equation for the salt flux:

\[
Q = \pi r_0^2 \left( -D \frac{\partial C}{\partial x} + vC \right).
\]  

Fig. 1. Working scheme and salt concentration distribution along capillary with subsaturation (1) and supersaturation (2) near the mouth (3 is the crystallization zone).

Capillary narrowing by a growing crystal for $\gamma = 2.4$ (1); $4.8$ (2); $7.2$ (3).

The boundary conditions are $C(0) = C_0$, $C(L) = C_m$ and $dC/dx(0) = 0$.

If $C_m < C_s$, the salt flux in the stationary state is zero; the solution to (2) here gives for $C_m =$ constant the standard expression [1, 2]

$$C_m = C_0 \exp(\alpha L/D).$$

Curve 1 in Fig. 1 shows the corresponding $C(x)$; at higher evaporation rates, $C_m$ may attain $C_s$, which allows a crystal to form and grow; experiment shows that the crystallization is heterogeneous, at the capillary walls [3]. We assume for simplicity that a crystalline phase is formed as shown in Fig. 1 in a certain zone of constant length $\ell$. The crystal is assumed to grow in layers, so the channel gradually narrows to $r < r_0$. Then $r_0 - r$ characterizes the layer thickness. The situation ceases to be stationary, since the crystal grows for a time $t$, so the flux $Q$, flow speed $v$, and radius of the free part $r$ are functions of time.

Here we give a solution for the growth beginning when $C_m$ becomes equal to $C_s$ at the end of zone $\ell$, i.e., at $x = L - \ell$; that state occurs after about $\Delta t = 2C_s D/3C_0 \alpha^2$, and during the subsequent evaporation, the concentration in $\ell$ begins to exceed $C_s$, so a crystal can form and grow.

The growing crystal reduces the evaporation area, so (2) is rewritten as

$$Q = \pi r_0^2 \left[ -D \frac{dC}{dx} + \alpha C \left( \frac{r}{r_0} \right)^2 \right].$$

Here $v$ is expressed in terms of the evaporation rate as the fluxes are equal: $\pi r_0^2 v = \pi r^2 \alpha$; the evaporation flux is proportional to $\pi r^2$, so any reduction in $\alpha$ reduces the flow speed. For each $t$, the solution to (4) in the quasistationary approximation for the salt flux to the meniscus is

$$Q_m(t) = \left( \alpha r^2 \right) \frac{C_s - C_0 \exp(\alpha r^2 L/r_0^2 D)}{1 - \exp(\alpha r^2 L/r_0^2 D)}.$$

$Q_m$ is a function of the current radius $r(t)$; the boundary condition is that the concentration at the entry to the crystallization zone is equal to the saturation concentration $C_s =$ constant (curve 2, Fig. 1). $Q_m(t)$ is consumed in altering the crystal mass $M_c$ and the dissolved substance mass $M_d$ in zone $\ell$. $C_m$ there is taken as constant (matched zone 3 in Fig. 1), so we have

$$Q_m(t) = \frac{d(M_c + M_d)}{dt} = \frac{d}{dt} [\pi (r_0^2 - r^2) \rho l + \pi r^2 C_m(t)].$$

The growth rate in $\ell$ is determined by the mass transfer coefficient $\beta$:

$$\frac{dr}{dt} = -\frac{\beta}{\rho} [C_m(t) - C_s].$$

If $C_m$ equals $C_s$, the crystal is in equilibrium and $dr/dt = 0$; for $C_m(t) \neq C_s$, the crystal either grows or dissolves.

System (5)-(7) represents the volume change; we introduce dimensionless variables and parameters for convenience: $z = r/r_0$; $\tau = t/t_0$; where $t_0 = 2\rho \ell/C_0 \alpha$; $\gamma = C_m(t)/C_s$; $\gamma = \alpha L/D$; $\lambda = C_s/C_0 > 1$; $\varepsilon = C_s/\rho$; $\nu = C_0 \beta t_0/\rho \tau_l$. Then (5)-(7) becomes