QUESTION OF STEFAN FLOW IN LIQUIDS

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Stefan flow equations are derived for aqueous electrolyte solutions. Experimental results are presented.

As is well known, the processes of mass transfer in vapor–gas mixtures in the presence of semipermeable surfaces are complicated by a penetrating flow component supplementing the fixed flow; this component has been termed Stefan flow by investigators [1-3].

Significant interest has developed recently in transfer phenomena occurring in liquids flowing under analogous conditions.

Such conditions are found universally in the processes of condensation or evaporation from solutions of acids, bases, or salts, and the approaches taken toward this problem have not always been valid. Thus, [4] considered liquid diffusion under conditions of semipermeability, but Stefan flow was not considered. In [5], the limiting case of pure diffusion without convective phenomena was considered, with the minimum possible evaporation rate being achieved, as is confirmed in the present study. The experimental studies of [6] found an anomalously low concentration change during mass transfer in a porous medium saturated by an electrolyte. To clarify that anomaly, the study proposed a hypothesis of additional mass transfer by diffusion through gaseous inclusions in the matrix. Such a process can actually occur during diffusion, but the investigators did not consider Stefan flow in the electrolyte. In [7], another transfer mechanism was considered in an electrolyte–porous matrix system. The effect of that mechanism reduces to the appearance in the matrix of a convective Stefan flow due to the capillary pressure drop occurring upon evaporation.

In calculating the operation of an electrical generating element, Tonkonogii introduced a convective term into the transfer equation and obtained a relationship which increased by a factor of 5-10 times the effective coefficient of diffusion of water in a porous matrix saturated by an electrolyte [8]. The author understood the term effective diffusion coefficient as the ratio of flow, with consideration of Stefan flow, to the concentration gradient.

In the above studies the question under discussion was put concretely, with reference to the operation of an electrical generating element, and in the convective phenomenon that was analyzed a general filtration of Stefan flow of the electrolyte developed because of the action of capillary forces.

However, Stefan flow is a basic property of semipermeability conditions, i.e., process conditions under which the phase boundary is impermeable to one of the solution components. Because of this generality, Stefan flow exists in liquid solutions having a free unbound state.

Therefore, it is of importance to derive the Stefan equation for liquids.

Derivation of the process equation will be performed under the following assumptions:

1) Upon change in solution concentration the total solution volume remains equal to the sum of the component volumes;

2) the solution temperature is constant;

3) the diffusion coefficient is independent of concentration.

We will assume a concentration range such that the liquids are mutually soluble.

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It is easly shown that in a solution of two liquids, when assumptions 1) and 2) are fulfilled, the concentration of one substance is linearly dependent on the concentration of the other.

We will consider a certain volume filled by a solution of two liquids. Let V_1 be the volume occupied in the solution by liquid 1 with a density γ_1 before mixing: $(V - V_1)$ is the volume occupied by liquid 2 with density γ_2 before mixing. The component concentrations in the solution will then be

$$\frac{V_1\gamma_1}{V} = c_1; \ \frac{(V - V_1)}{V}\gamma_2 = c_2.$$

From these two equations there follows the linear dependence

$$c_1 = \gamma_1 - bc_2, \tag{1}$$

where γ_1 and $b = \gamma_1/\gamma_2$ are constants.

The applicability of Eq. (1) rests on the real relationship between the partial densities of the solution components, which is shown in Fig. 1. Of the six aqueous electrolyte solution characteristics shown in Fig. 1, five have characteristics close to linear joining the endpoints of each of the curves. Nonlinearity appears especially strongly in the case of the sodium hydroxide solution. The effect of nonlinearity will be considered below.

As follows from [9], a relationship quite close to Eq. (1) is valid in a significant number of cases.

We will consider the case of evaporation from an aqueous solution of one electrolyte. We direct the x axis from the phase boundary into the depths of the solution. Component 2 has a low vapor pressure and undergoes practically no evaporation, so that the phase boundary is impermeable for it.

On the evaporation surface ($x = 0$) the concentration of the evaporating component is lower than in the depth of the solution. In view of Eq. (1), the concentration of component 2 is higher at the solution surface than in the depth, so that, following the diffusion laws, component 2 should diffuse into the body and be liberated from the solution. However, the quantity of component 2 in the solution does not change. Under these conditions, with the Stefan assumption there should exist a general flow of the mixture in the direction of the penetrating component, compensating the diffusion flow of the nonevaporating component.

Since the Fick diffusion law is completely applicable to a solution of a single electrolyte [10], we may write

$$-j_1 = wc_1 + D_1\frac{dc_1}{dx}, \tag{2}$$

$$-j_2 = wc_2 + D\frac{dc_2}{dx} = 0. \tag{3}$$

Considering Eqs. (2), (3), and (1), we obtain

$$j_1 = \frac{\gamma_1 D dc_2}{c_2 dx}. \tag{4}$$

Integrating Eq. (4) between the limits $x = 0$ and $x = s$, we finally have

$$j_1 = -\frac{\gamma_1 D}{s}\ln\frac{c_{20}}{c_{2s}}. \tag{5}$$

Equation (5) was obtained from the linear relationship between component concentrations in the solution. In an accurate description of the curve $c_1 = f(c_2)$ for an aqueous solution of sodium hydroxide, the quantity b would be taken as a function of c_2, i.e., $c_1 = \gamma_1 - b(c_2)\cdot c_2$, where $b(c_2) = -0.388c_2^2 + 0.762c_2 - 0.0622$. The mass flow calculated with this exact curve differs from the mass flow using linear equation (1) for NaOH by not more than 10%. For the other solutions considered in Fig. 1, the error in the flow due to nonlinearity does not exceed 4%.

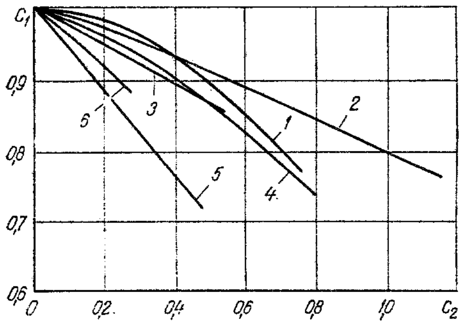

Fig. 1. Actual relationships between component concentrations in solution; c_1) water concentration, g/cm^3; c_2) solute concentration, g/cm^3; 1) NaOH; 2) $AgNO_3$; 3) NaBr; 4) KOH; 5) HCl; 6) KCl.

We will write the Fick equation for the present case in integral form:

$$j_1 = -\frac{D}{s}(c_{1s} - c_{10}). \tag{6}$$

For one and the same values of c_{1S} and c_{10} the ratio between the flow calculated with Stefan equation (5) and the flow calculated by the Fick law (6) comprises

$$\frac{j_S}{j_F} = \frac{\gamma_1}{c_{1s} - c_{10}} \ln \frac{c_{20}}{c_{2s}}. \tag{7}$$

Using Eq. (1) to express c_2 in terms of c_1, we obtain

$$\frac{j_S}{j_F} = \frac{\gamma_1}{m}, \tag{8}$$

where $m = [(\gamma_1 - c_{10}) - (\gamma_1 - c_{1S})]/\ln[(\gamma_1 - c_{10})/(\gamma_1 - c_{1S})]$ is the mean logarithmic difference of the quantities $(\gamma_1 - c_{10})$ and $(\gamma_1 - c_{1S})$; $\gamma_1 \approx 1$ g/cm^3 is the density of water.

It is evident from Eq. (8) that the ratio j_S/j_F drops sharply with decrease in the total solvent content in the solution and that for high-concentration solutions it is close to unity.

We will present the well-known Stefan equation for vapor condensation from a vapor–gas mixture:

$$j_1 = \frac{DP_{\text{mix}}}{R_v T s} \ln \frac{P_{20}}{P_{2s}}. \tag{9}$$

Comparing Eq. (5) with Eq. (9), we see their identical form. In fact, in Eq. (9) the complex $P_{\text{mix}}/R_v T$ is none other than a certain effective specific gravity of the pure vapor at temperature T and pressure P_{mix}. The ratio of partial pressures of the noncondensing gas may be represented as the ratio of its partial pressures at the mixture temperature.

Equation (5), like Eq. (9), contains a limitation on the magnitude of the component partial densities. The partial density of the nonevaporating material in Eq. (5) can be no larger than the value determined from the condition of solubility. In Eq. (9), the vapor density cannot exceed the value determined by the saturation temperature, equal to the mixture temperature.

Considering Eqs. (3) and (4), we note that for a solution with a free state the displacement rate of the phase boundary upon evaporation or condensation is equal to the Stefan flow velocity in the liquid.

We will clarify this statement.

We imagine a vessel, the bottom of which is a piston, containing an evaporating solution. To maintain the phase boundary at a specified level, the piston must move at some velocity w_p. From Eq. (3), the Stefan flow velocity takes on the value $(D/c_2)(dc_2/dx)$.

Considering Eq. (4), we obtain

$$j_1 = \gamma_1 w. \tag{10}$$

Not taking account of the differential expressions, it follows from elementary considerations that in the case with the piston $j_1 = \gamma_1\omega_p$, i.e., the same as Eq. (10), inasmuch as j_1 and γ_1 are one and the same.

In a special case the role of the piston may be fulfilled by capillary forces. If the piston is immobile, the phase boundary will descend with the same velocity w.

Under conditions of semipermeability, the density of the mass flow in a vapor–gas medium will have the same external form as Eq. (10), since with unchanging barometric pressure and constant temperature the vapor–gas mixture, down to the saturation point, obeys Eq. (1) much more exactly than liquids do:

$$j_1 = \gamma_v w_g. \tag{11}$$

In the processes under consideration we have neither mass sources nor sinks. For one and the same mass-transfer process between electrolyte and vapor–gas mixture, Eq. (11) may be set equal to Eq. (10). As a result,

$$w_g = \frac{\gamma_1}{\gamma_v} w, \tag{12}$$

i.e., in evaporation from a solution or condensation on its surface the Stefan flow rate in the vapor–gas mixture is as many times larger than the Stefan flow rate in the liquid as the effective density of the pure solvent is larger than the effective density of the vapor, determined by the pressure and temperature of the process.

We will demonstrate the importance of considering Stefan flow in liquids in solution of practical problems by presenting experimental results obtained with hydrated calcium oxide.

The experimental apparatus for study of heat and mass transfer under conditions of semipermeability (Fig. 2) consisted of three main components: the body 2 and sleeves 5 and 9. Channels were milled in the sleeves for the heat-transfer agent 4 (KOH) and the distillate 8. On the open end of the KOH channels porous metalloceramic elements 1 and 7, 63 mm in diameter, were attached. These served as the phase boundaries, and a vapor–gas space 3 was formed between them, through which mass transfer from the alkali solution to the distillate occurred. The upper sleeve was rigidly fixed to a shaft, held in a sliding bearing and movable in the body opening. The stem of dial indicator 6, type ICh-10, was attached to the shaft to measure the size of the vapor–gas space. The accuracy of this measurement varied with scale position from 6 μm at the bottom of the scale to 20 μm at the top. To determine zero spacing, an electrical potential was applied across the porous elements so that a bulb lit up when they made contact. The temperature of the heat-transfer agent was measured by thermocouples coated with OÉP-41-71 epoxy resin. In the experiments, the heat-transfer agent was circulated through closed channels by special pumps. Flow rate was measured by RS-3 rotameters. Each channel was totally closed and communicated with the external atmosphere only through a measurement cylinder calibrated every 0.2 ml. Thus, the change in liquid level in the measurement cylinders was used to determine the water mass flow transferred from the alkali to the distillate. The distillate-saturated porous element used was able to withstand the pressure head without loss of water seal, permitting vacuum charging of the system with the working agents. It should be noted that the porous elements were soaked in water after the system was evacuated of air.

The porous element used in the experiment had a diffusion attenuation coefficient $\mu = 5$, and its thickness was 0.5 mm. The following parameters were maintained in the experiments: $t_{el}^{in} = 80°C$; $t_{ca}^{in} = 60°C$; $G_{el} = G_{ca} = 35$ kg/h; and $\alpha_{el} \approx \alpha_{ca} = 1100$ kcal/m²h·deg. The pressure of the vapor–gas mixture in the gap between the porous elements was maintained at a level of 1.3 kg/m² and measured by a reference manometer [GOST (All-Union State Standard) 6521-60]. A KOH concentration of 20% by weight was maintained practically constant by the inclusion of additional volume in the circuit through which the electrolyte was pumped. Samples of liquid were taken for testing from the channels before and after the experiment.

The density of the samples was determined by densimeters (GOST 1300-57). The entire experiment lasted 12 h. Over this time the KOH concentration in the alkali channel increased

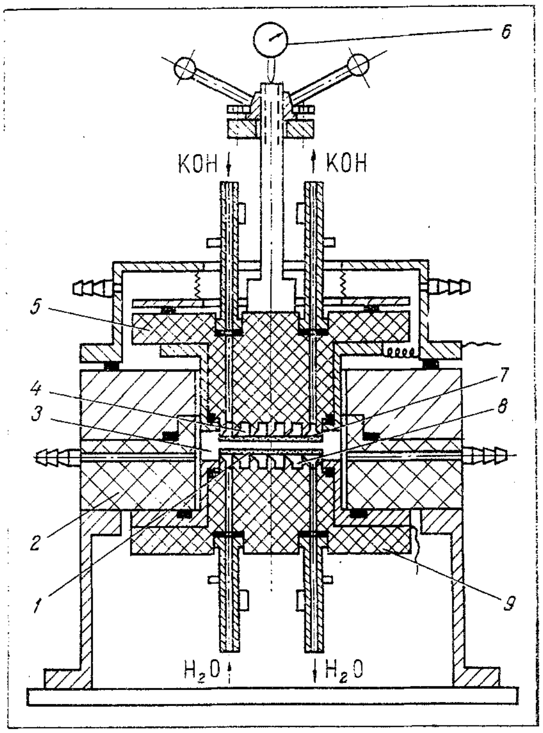

Fig. 2. Experimental apparatus: 1) porous element; 2) body; 3) gas–vapor space; 4) alkali channel; 5) movable sleeve; 6) dial indicator; 7) porous element; 8) distillate channel; 9) fixed sleeve.

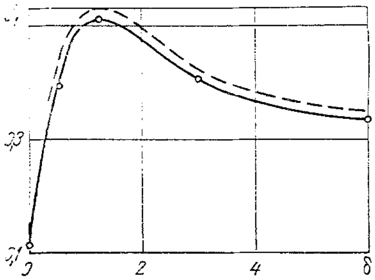

Fig. 3

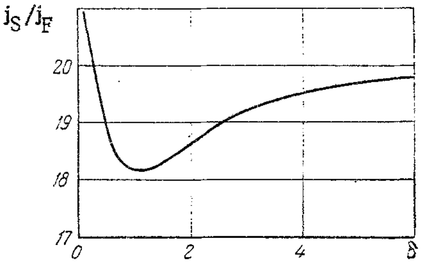

Fig. 4

Fig. 3. Solvent flow density J_1 (g/cm²·h) versus size of vapor–gas space δ (mm); solid line) experiment; dashed line) calculation.

Fig. 4. Ratio of solvent flow with consideration of Stefan flow in electrolyte to solvent flow calculated purely from Fick's law as a function of vapor–gas space size δ, mm.

by 1%. No alkali was detected in the water circuit.

The experimental results are shown by the solid line of Fig. 3. In the experiments each value of vapor–gas space corresponded to a unique water flow and electrolyte concentration shift across the porous element. Flow values close to experimental were obtained by calculation (dashed curve of Fig. 3). To do this, the full system of heat- and mass-transfer equations describing the experimental process must be solved. In doing this the electrolyte diffusion process must be described by Eq. (5) with consideration of attenuation of the diffusion coefficient.

The ratio j_S/j_F for the existing experimental [i.e., those calculated with Eq. (5)] electrolyte concentration shifts in the porous element are shown in Fig. 4.

It follows from the figure that in electrolytes the solvent flow calculated with consideration of Stefan flow may be 18-20 times larger than the solvent flow calculated solely by the Fick equation.

Thus, in processes of mass transfer between an electrolyte containing a component with a low vapor pressure and a vapor–gas medium, Stefan flow in the electrolyte is of significant importance and must be considered in practical calculations.

NOTATION

c, concentration of material in solution; j, solvent flow density; w, Stefan flow velocity in liquid; D, coefficient of molecular diffusion; j_S, solvent flow density with consideration of Stefan flow; j_F, solvent flow density determined solely by Fick's law; P_{mix}, pressure of vapor–gas mixture; R_v, gas constant of water vapor; T, temperature of process; P, partial pressure; w_g, Stefan flow velocity in vapor–gas medium; γ_v, effective specific gravity of water vapor, $\gamma_v = P_{mix}/R_vT$; α, heat-transfer coefficient; G, heating-agent flow rate; δ, thickness of vapor–gas space. Indices: 1) movable component; 2) fixed component; 0) on phase boundary; s) at distance s from phase boundary; el) electrolyte; ca) cooling agent; in) at input of evaporator or condenser.

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