LOCAL HEAT TRANSFER IN DISSOCIATING
# ACETIC ACID VAPOR

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Experimental results are presented for the local heat transfer in a heated turbulent flow of dissociating acetic acid vapor. The experimental data are generalized by two methods.

Although to date heat transfer in the presence of chemical reactions has been reliably investigated only for dissociating nitrogen tetroxide, N_2O_4 [1-10], this problem is directly relevant to the design of reaction equipment of various kinds used in the chemical industry; in designing such equipment, present practice is to disregard the effect of the reaction, which can be very significant [11]. Evidently, therefore, there is a need for investigations of the convective heat transfer in various chemically reacting systems.

The present work is devoted to an experimental investigation of the local convective heat transfer in a turbulent flow of dissociating acetic acid vapor. At atmospheric pressure, saturated acetic acid vapor consists predominantly of dimers [12]. Heating leads to breaking of two hydrogen bonds and conversion of the dimers to monomers. Comparison of the chemical-relaxation time and the residence time of the vapor in the experimental apparatus showed that the formation and decomposition of dimers may be regarded as a reversible equilibrium chemical reaction:

$$(CH_3COOH)_2 \rightleftharpoons 2CH_3COOH - 58.6 \text{ J/mole}. \tag{1}$$
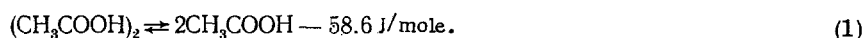
The experimental apparatus and procedure, together with some of the results, were described in [13, 14]. In the experiments, the basic parameters were varied in the following ranges: $Re_w = (8-47) \cdot 10^3$; $q_w = (8-64) \cdot 10^3$ W/m²; $t_{fl} = 130-330°C$; and $t_w = 155-410°C$. All the experiments were carried out at atmospheric pressure. Altogether, the results of 62 experiments were analyzed and, for eight sections of the experimental apparatus, 496 experimental points were obtained. The calculations were carried out on an Odra-1204 electronic calculator. To eliminate end effects, the data were analyzed for the central position of the experimental channel, from $x/d = 30$ (section 1) to $x/d = 100$ (section 8).

In one of the experiments, the mean-mass temperature of the dissociating vapor was measured in three intermediate sections of the experimental channel, switching off sections of the electrical heater as described in [2]. Each of these measurements was made three times; the discrepancy between the calculated and measured flow temperatures in these sections did not exceed 3-5% of the temperature drop between the outlet and the inlet of the experimental channel.

The experimental material obtained showed that the change in t_w, t_{fl}, and α_e over the length of the reaction channel resembles the change in these values found earlier [1-7] for a turbulent flow of steadily dissociating nitrogen tetroxide. Only in [10] does the curve $t_{fl} = f(x/d)$ have a somewhat different form. From an analysis of the experimental data it appears that the heat transfer is significantly affected by the hydrodynamics of the dissociating flow. Thus, the heat-transfer coefficients found in our experiments varied from 163 W/m²·°C for $Re_w = 9.9 \cdot 10^3$ to 1123 W/m²·°C for $Re_w = 46.6 \cdot 10^3$.

To elucidate the effect of q_w and $t_{fl,in}$ on α_e the curves in Fig. 1 were plotted. In Fig. 1a, curves of $\alpha_e = f(x/d)$ are shown for four experiments with approximately equal $t_{fl,in}$ and Re_w, but different q_w. From these
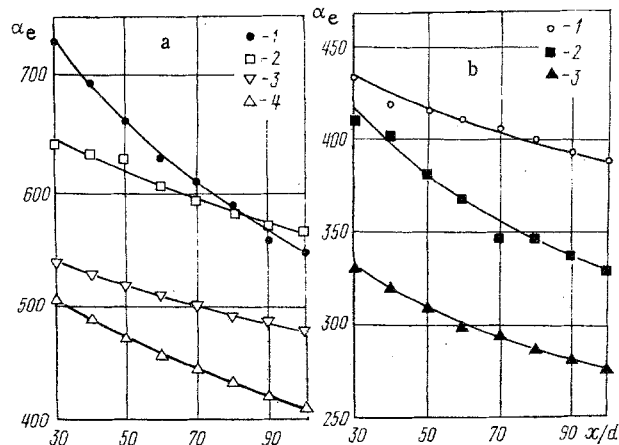
Fig. 1. Change in heat-transfer coefficient over
the length of the experimental channel: a) $t_{fl,in} =$
149.9 (1), 149.2 (2), 150 (3), and 150°C (4); $Re_w =$
$(29.7-28.5) \cdot 10^3$ (1), $(29.6-27.2) \cdot 10^3$ (2), $(29.2-$
$26.5) \cdot 10^3$ (3), and $(27.8-24.3) \cdot 10^3$ (4); $q_w = (9.8-$
$10) \cdot 10^3$ (1), $(20.6-21.2) \cdot 10^3$ (2), $(26.6-27.5) \cdot 10^3$
(3), and $(32.0-33.7) \cdot 10^3$ W/m^2 (4); b) $t_{fl,in} = 130.2$
(1), 150.0 (2), and 170.1°C (3); $Re_w = (21.6-19.3) \cdot$
10^3 (1), $(20.2-17.8) \cdot 10^3$ (2), and $(18.2-16.0) \cdot 10^3$
(3); $q_w = (22.0-22.9) \cdot 10^3$ (1), $(23.4-24.6) \cdot 10^3$ (2),
and $(23.8-25.2) \cdot 10^3$ W/m^2 (3).

curves it is evident that the heat-transfer coefficient α_e depends significantly on the specific heat flux q_w: With
increase in q_w, α_e falls. This is a result of the change in thermophysical properties at high q_w (and, of course,
also t_{fl}) far from the maximum.

In Fig. 1b, curves of $\alpha_e = f(x/d)$ are plotted for three experiments with similar Re_w and q_w but different
$t_{fl,in}$. It is evident from Fig. 1b that increase in $t_{fl,in}$ leads to decrease in α_e, which is explained in this case
by the change in thermophysical properties of the dissociating acetic acid vapor. The rise in t_{fl} of the disso-
ciating vapor over the length of the experimental channel leads to some decrease in Re_w associated with the in-
crease in dynamic viscosity. The fall in Re_w, in turn, causes a decrease in α_e over the length of the reaction
channel.

To estimate the effect of the dissociation of the acetic acid vapor on the heat transfer, experimental
values α_e were compared with the calculated "frozen" value α_f. It was found that the experimental heat-trans-
fer coefficient may exceed the corresponding heat-transfer coefficient for the nonreacting gas by a factor of
2-8. The variation of α_e/α_f in [2, 8, 9] was also approximately in this range. Hence it is clear that the effect
of the reaction must be taken into account in calculating the surface heat transfer in various kinds of reaction
equipment used in the chemical industry. The "frozen" values of the heat-transfer coefficient α_f were cal-
culated according to the well-known formula of [15].

The Lewis—Semenov number Le for dissociating acetic acid vapor, calculated according to [16], was found to
differ insignificantly from unity in the temperature range covered by our experiments (Le = 0.8-1.25). Note that the
temperature dependence and the range of variation of Le for the system $(CH_3COOH)_2 \rightleftharpoons 2CH_3COOH$ converges
with that for the other equilibrium system $N_2O_4 \rightleftharpoons 2NO_2$ [17].

The experimental data obtained for the heat transfer in dissociating acetic acid vapor were generalized
in the coordinates

$$\lg \frac{Nu_{w,ef}}{Pr_{w,ef}^{1/3}} \cdot \frac{c_{pw,ef}}{\bar{c}_{p,ef}} - \lg Re_w$$

in agreement with the procedure proposed in [3] for the thoroughly investigated equilibrium dissociating system
$N_2O_4 \rightleftharpoons 2NO_2$. For brevity, calculations were carried out only for four sections of the experimental apparatus
(x/d = 30, 50, 70, and 100), but the whole of the central portion of the experimental channel was covered. From
Fig. 2 it is evident that for most of our experimental points (about 95%) the scatter around the mean was ±15%, the
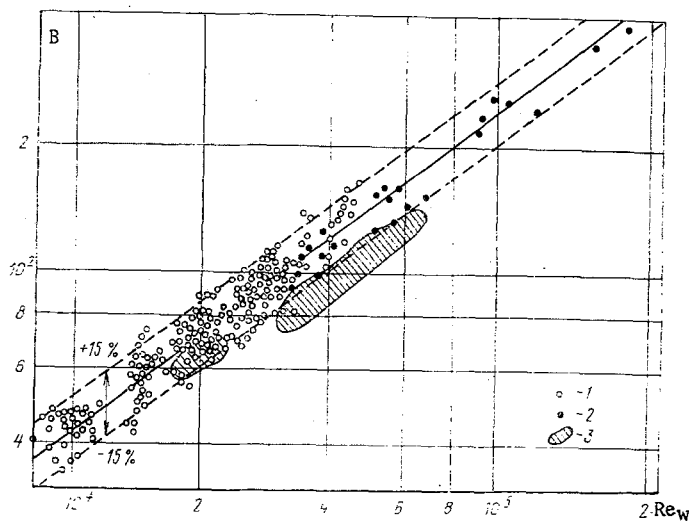maximum scatter being ±18%. On this basis, the following relation was obtained:

Fig. 2. Generalization of experimental data by the method of [3] for the systems $(CH_3COOH)_2 \rightleftharpoons 2CH_3COOH$ (1), [2] (2), $N_2O_4 \rightleftharpoons 2NO_2$ and $N_2O_4 \rightleftharpoons 2NO_2$ [3] (3). $B = (Nu_{w,ef}/Pr_{w,ef}^{1/3})(c_{pw,ef}/\bar{c}_{p,ef})$.
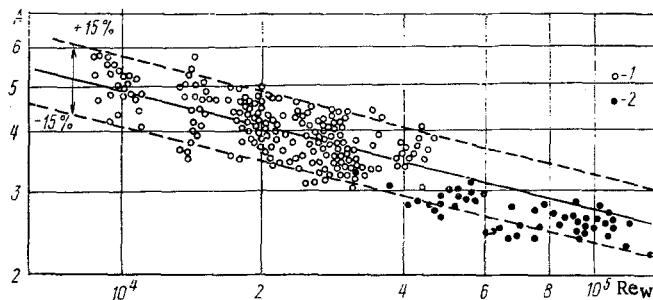

Fig. 3. Generalization of the experimental data using the procedure of [2] for the systems $(CH_3COOH)_2 \rightleftharpoons 2CH_3COOH$ (1) and $N_2O_4 \rightleftharpoons 2NO_2$ [2] (2). $A = St_{ef}[k_1(\xi_w) + k_2(Pr_{w,ef})\sqrt{\xi_w/8}(Pr_{w,ef}^{2/3}-1)] \cdot 10^3$.

$$Nu_{w,ef} = 0.053\, Re_w^{0.73} Pr_{w,ef}^{1/3}\, \frac{\bar{c}_{p,\,ef}}{c_{pw,\,ef}}. \qquad (2)$$

It is of some interest to compare our data on the heat transfer in equilibrium dissociating acetic acid vapor with experimental data on the other equilibrium dissociating system $N_2O_4 \rightleftharpoons 2NO_2$, which has been much studied, especially for the case of turbulent flow [1-10]. Earlier experimental material of the Institute of Nuclear Energy of the Academy of Sciences of the Belorussian SSR was treated at the Institute of High Temperatures of the Academy of Sciences of the USSR by the method of Petukhov et al. [4]. Satisfactory agreement was found between the results obtained at the two institutes. Therefore, for our purposes it is sufficient to carry out the generalization of the experimental data on the system $(CH_3COOH)_2 \rightleftharpoons 2CH_3COOH$ with any one group of experimental data on the system $N_2O_4 \rightleftharpoons 2NO_2$. To this end, the experimental data of [2] and the results of [3] are plotted in Fig. 2, from which it is evident that both our data and those of the Institute of High Temperatures [2] are well described by Eq. (2).

It is also evident from Fig. 2 that Eq. (2) satisfactorily describes the data of [3] for Re_w around $2 \cdot 10^4$, while for Re_w between $3 \cdot 10^4$ and $4.6 \cdot 10^4$ it lies approximately 15% below. Thus, a single relation — Eq. (2) — describes the experimental data on heat transfer in two different equilibrium reactions.

In addition, one further generalization of the experimental data was carried out, this time using the method developed at the Institute of High Temperatures by Petukhov et al. [2]. From the generalization obtained (Fig. 3), it appears that the results of our measurements are grouped with a scatter of ±15% about the mean line for the majority (about 95%) of the experimental points, the maximum scatter being ±18%. Like the previous

calculations, these were restricted to the central section of the experimental channel (x/d = 30, 50, 70, and 100). The generalized dependence takes the form

$$St_{ef} = \frac{1.25\,\xi_w/8}{k_1(\xi_w) + k_2(Pr_{w,ef})\,\sqrt{\xi_w/8}\,(Pr_{w,ef}^{2/3} - 1)},\qquad(3)$$

where

$$\xi_w = (1.82\lg Re_w - 1.64)^{-2},$$
$$k_1(\xi_w) = 1 + 3.4\,\xi_w$$
$$k_2(Pr_{w,ef}) = 11.7 + \frac{1.8}{Pr_{w,ef}^{1/3}}.$$

In [2], in contrast to our result, the constant coefficient in the right-hand side of Eq. (3) was 1.1. In generalizing the experimental data, effective values of the thermal conductivity and specific heat of the dissociating acetic acid vapor were used; $c_{p,ef}$ was calculated by the method outlined in [1], while λ_{ef} was chosen according to the experimental data of [18]. The numbers $Nu_{w,ef}$, Re_w, and $Pr_{w,ef}$ were calculated according to the physical properties referred to the wall temperature. In addition to our data, Fig. 3 also shows experimental data on the heat transfer for the equilibrium dissociation of nitrogen tetroxide [2].

Thus, generalizing the experimental data on heat transfer for two different equilibrium dissociating systems shows that both may be described by Eqs. (2) and (3). These equations may also be used to calculate the heat transfer for other, as yet unstudied, equilibrium dissociation reactions with Le $\approx$ 1 and other parameters in the appropriate ranges.

NOTATION

x   is the tube length, m;
d   is the internal diameter of tube, m;
q   is the specific heat flux, W/m²;
t   is the temperature, °C;
α is the local heat-transfer coefficient, W/m²·°C;
λ is the thermal conductivity, W/m·°C;
c_p is the true specific heat at constant pressure, J/kg·°C;
$\bar{c}_p$ is the mean specific heat at constant pressure, J/kg·°C;
ξ is the frictional-drag coefficient;
Nu   is the Nusselt number;
St   is the Stanton number;
Re   is the Reynolds number;
Pr   is the Prandtl number;
Le   is the Lewis number.

Indices

e   is the experimental;
ef   is the effective;
f   is the frozen;
w   is the wall;
fl   is the flow;
in   is the channel inlet.

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DISTRIBUTION OF DISSOLVED GAS IN WATER AND BUBBLES IN ICE UPON MOVEMENT OF A CRYSTALLIZATION FRONT

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The distribution of dissolved gas in water upon increase in a crystallization front is considered. Optimal conditions are derived for water crystallization, under which the gas-bubble distribution in the ice formed will be the most homogeneous.

As is well known [1], the solubility of air in water is at least an order higher than its solubility in ice. Thus, upon crystallization of water at the phase boundary the dissolved air is liberated and diffuses into the water volume and partially into the ice. Thus, in both the water and the ice the air solution becomes supersaturated. Usually, the water contains a number of particles of a different substance, which may become centers of gas-bubble formation at relatively low supersaturations. Gas bubbles are formed ahead of the crystallization front on these centers. With increase in supersaturation, the number of active bubble-formation centers increases. Therefore, the structure of the ice formed by crystallization of water will be determined by the degree of supersaturation of the solution ahead of the crystallization front, which, in turn, is dependent on the gas-liberation rate at the crystallization front. With increase in crystallization-front displacement