Corresponding Member of the Academy of Sciences of the USSR B. V. DERYAGIN, S. V. NERPIN,

M. A. ARUTYUNYAN

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR B. V. DERYAGIN, S. V. NERPIN,
M. A. ARUTYUNYAN

ON THE MECHANOCALORIC EFFECT AT ORDINARY TEMPERATURES

When liquids flow through a porous partition, two effects are of particular interest: the mechanocaloric effect—the appearance of a temperature difference ΔT on the two sides of the partition at a given pressure difference ΔP—and the thermomolecular effect (thermo-osmosis)—the appearance of a pressure difference ΔP at a given temperature difference ΔT.

The thermodynamics of irreversible processes (1,2) leads to the following relation between these effects:

$$\frac{d\Delta P}{d\Delta T} = -\frac{Q^*}{vT}, \tag{1}$$

where v is the molar volume; T is the absolute temperature; Q^* is the heat of transfer, equal to $U^* - w$; U^* is the specific energy of transfer, i.e., the energy transported by unit mass; w is the specific enthalpy of the bulk liquid.

A necessary condition for the existence of both effects is $Q^* \neq 0$, i.e., $U^* \neq w$.

In the case of bulk flow of a liquid, $U^* = w$, $Q^* = 0$, and the effects of interest to us are equal to zero.

However, a liquid or gas flowing through a porous partition is in the field of surface forces, the total action of which depends on the specific surface area of the given porous medium. It is known that surface forces are capable of changing the structure of a liquid lying within their sphere of influence (3), and this may entail a change in the specific enthalpy as compared with a bulk liquid of unchanged structure. If it is assumed that the surface layers are not rigidly bound to their solid substrate, but retain fluidity, then in this case, when a gas or liquid flows through a porous partition, one may expect that $Q^* \neq 0$, i.e., $U^* \neq w$.

Fig. 1. Schematic of the apparatus for investigating the mechanocaloric effect

Thus, the mechanocaloric and thermomolecular effects during the flow of a liquid through a porous partition with relatively small pores may be nonzero.

Fig. 1. Schematic of the apparatus for investigating the mechanocaloric effect

Figure 1: Fig. 1. Schematic of the apparatus for investigating the mechanocaloric effect

Fig. 2. Dependence of ΔT on the water flow rate

Figure 2: Fig. 2. Dependence of ΔT on the water flow rate

The scheme of the apparatus for the experimental study of the mechanocaloric effect is shown in Fig. 1. With the aid of valves 5, the liquid could be driven both from vessel A into B, and conversely. The system was thermostatted. The liquid level in vessels 1 was kept constant.

The liquid flow rate was measured with a graduated vessel 6. The mechanocaloric effect was measured by means of a battery of 100 series-connected thermocouples 3, connected to a highly sensitive galvanometer 2; the junctions of the thermocouples a and b were arranged so that, in one case, junctions a were in the immediate vicinity of the partition 4 (a fine-pored glass filter), while b were at a distance of several centimeters, but on the same side of it (Fig. 1); in the other case, junctions a and b, being in the immediate vicinity of the partition, were placed on different sides of it.

The results of experiments with water are shown in Fig. 2, where along the ordinate is plotted the change in temperature ΔT due to the presence of ΔP, and along the abscissa—the liquid flow rate (the amount of water passing through the partition per unit time). Straight line I characterizes the process when the liquid flows from A to B, when the thermocouple junctions are arranged as shown in Fig. 1, and $T_a - T_b = \Delta T < 0$. Straight line II refers to the process with the same arrangement of thermocouples, but with the opposite direction of water flow; in this case $T_a - T_b = \Delta T > 0$.

Fig. 2. Dependence of ΔT on the water flow rate

If straight line I characterizes the mechanocaloric effect proper, then straight line II, obviously, characterizes the total effect: the effect under study plus Joule heat arising when the liquid flows through the capillary system.

Straight line III is the experimental line obtained for the case in which the thermocouple junctions were arranged on different sides of the partition. The effect here is greatest, since an increase in temperature at some junctions is associated with a decrease at others, whereas in the case of arranging all junctions on one side of the partition the temperature at the b junctions (Fig. 1) was constant.

As is seen from the graph (Fig. 2, I), the dependence $\Delta T = f(J)$ is linear, which agrees with the theory of the mechanocaloric effect set forth in [2]:

$$J = \frac{\Delta T}{T} \int_0^\infty \frac{\Delta wh\, dh}{\eta} \sum_i \frac{S_i}{l_i}, \tag{2}$$

where J is the total liquid flux through the pores of the filter; Δw is the change in the specific enthalpy of the liquid as a function of the distance h from the solid substrate; η is the viscosity of the liquid; S is the cross-sectional area of an elementary pore; l is the length of an elementary pore.

Equation (2) may be rewritten in the form

$$\Delta T = kJ, \tag{2'}$$

where

$$k = \frac{T}{\displaystyle\int_0^\infty \frac{\Delta wh\, dh}{\eta} \sum_i \frac{S_i}{l_i}}.$$

Comparison of the experimental data with formula ($2'$), while giving good qualitative agreement (the presence of a linear dependence of ΔT on J), does not give entirely satisfactory quantitative agreement.

In particular, experimentally we were unable to detect ΔT at $J < 0.0023$ cm^3/s ($\Delta P < 50$ mm Hg).

It may be assumed that the surface layers, possessing a limiting shear stress, begin to flow at some $\Delta P > \Delta P_0$ (in our experiments $\Delta P_0 > 50$ mm Hg).

Institute of Physical Chemistry
Academy of Sciences of the USSR

Agrophysical Institute
All-Union Academy of Agricultural Sciences
named after V. I. Lenin

Institute of Deserts
Academy of Sciences of the Turkmen SSR

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