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Note

Dependence of the rate of water evaporation on the pressure of its vapour

A. P. CHUPAKHIN AND N. Z. LYAKHOV

Institute of Physico-Chemical Principles of Raw Material Processing, Siberian Division of the U.S.S.R. Academy of Sciences, Novosibirsk 630091, Derzhavina, 18 (U.S.S.R.)

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Some recent papers[1–5] by French scientists report the discovery of a complicated dependence of the evaporation rate of liquid water, v, on the pressure of its vapour, P_{H_2O} (Fig. 1, curve 1). The presence of extrema on the curve v–P_{H_2O} is attributed by these authors[1–5] to a complicated dependence of the heat conductivity coefficient of gas-phase water on P_{H_2O}, because they consider the limiting stage of the evaporation process to be the stage of heat-feed through the gas-phase to the surface of evaporating liquid, the temperature of which, due to the effect of self-cooling, is lower than that of the thermostat. The dependence of the rate of the dehydration reaction on P_{H_2O} has a similar form (with a minimum and maximum) for many crystallohydrates and is referred to as the Topley–Smith effect[6]. The qualitative coincidence of the functions of $v(P_{H_2O})$ for various processes led the authors of refs. 1–5 to the conclusion about

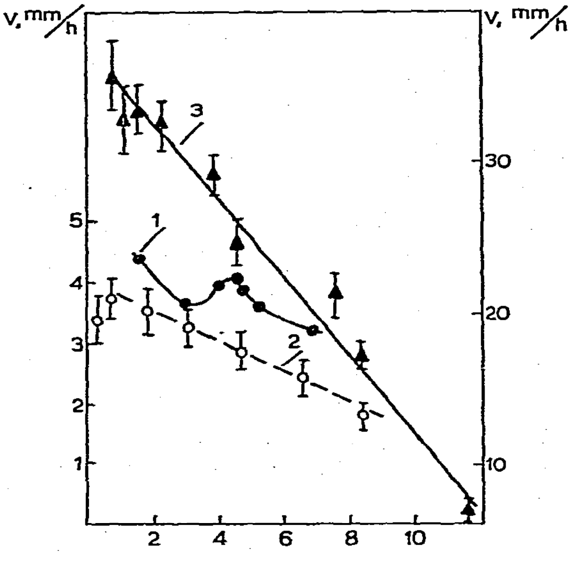

Fig. 1. Dependence of the rate of water evaporation on its pressure. The left-hand ordinate axis is for curves 1 and 2, the right-hand axis, for curve 3.

the universal character of the Topley–Smith effect which must occur in every endothermal process accompanied by the elimination of gases from the condensed phase.

The aim of the present work was to study the dependence of the rate of water evaporation on P_{H_2O} under the conditions providing the heat-feed through the condensed phase.

Note that the results reported in refs. 1 and 2 and those in refs. 3–5 essentially differ. In refs. 1 and 2, at a thermostat temperature of 20.5 °C, the minimum evaporation rate of 0.8 mm h^{-1} was observed at a vapour pressure of 0.5 mm Hg, the maximum, 2.3 mm h^{-1}, at 4.5 mm Hg, and the ratio $v_{max}/v_{min} = 2.9$. The data from refs. 3–5 for the temperature of 23 °C are given in Fig. 1; here $v_{max}/v_{min} = 1.15$ and the differences are not brought about by the temperature shift from 20.5 to 23 °C; this conclusion follows from the results for 5.5 °C which are also cited. The magnitude of the evaporation rate (later, reference will only be made to the more recent data from refs. 3–5) is larger by more than two orders of magnitude than in the classical works[7,8]: based on the value of the condensation coefficient determined from the Knudsen formula[7]

$$v = \frac{\alpha}{\sqrt{2\pi\, mkT}}(P_0 - P)$$

(m is the mass of a molecule; P is the gas pressure, P_0 is the equilibrium pressure at a temperature T), this gives a value of $\sim 10^{-4}$ which, even considering the overcooling on the interface, amounts to 15–20 °C, while according to the data from literature $\alpha \sim 10^{-2}$.

The rate of evaporation in refs. 3–5 was determined in an installation which is presented schematically in Fig. 2(a). From the vessel (1) placed in the thermostat at a temperature T_1, the water evaporates into a preliminary evacuated system and passes into a trap condenser (2), which is thermostabilized at a lower temperature T_2. The

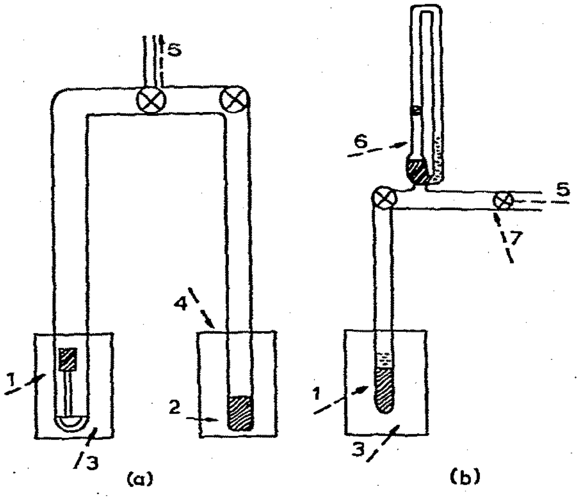

Fig. 2. Scheme of experimental installation. (1) vessel with evaporating water; (2) condenser; (3) and (4) thermostats; (5) pumping-out; (6) pressure gauge; (7) regulation tap.

rate of evaporation was measured by recording the displacement of the liquid–gas interface. By varying the temperature of the cold-point, T_2, in the system the authors obtained different P_{H_2O}-values which they believed to correspond to the equilibrium values at temperature T_2.

It is evident that, in the system described, three processes occur: evaporation, mass-transfer and condensation, and the pressure will correspond to the equilibrium pressure at temperature T_2, while the measured rate of evaporation will correspond to the real one, only when the limiting process is that of evaporation. It can readily be verified that the water mass-transfer is not a limiting process under these conditions. However, the P_{H_2O} values measured in our experiments with the help of an oil gauge exceeded by far the equilibrium values even with a more effective trap (2) (with a larger section and volume) than in refs. 1–5.

To eliminate the influence of the condensation process on the rate of evaporation the present authors used a pump instead of condenser (2), as shown in Fig. 2(b). In this case the water vapour pressure in the system was regulated by varying the pumping-out rate, by means of regulating tap (7), and checked by an oil gauge (6). The results obtained are depicted in Fig. 1, curve 2 referring to the case of an air thermostat (3), and curve 3, to that of a water thermostat. In both cases the temperature is 20.5 °C*.

The results obtained allow the following conclusions to be drawn.

(1) The value of evaporation rate, as was to be expected[7], greatly depends on the intensity of heat-feed to the interface (curves 2 and 3 were obtained at the same thermostat temperature but the heat-feed conditions were more effective in the case of curve 3).

(2) Nevertheless, within the dispersion range of experimental data the dependence of evaporation rate on pressure can be described by the Knudsen formula though the condensation coefficient determined from it is about one order lower than that known from literature[7, 8], and decreases with increase in the degree of deviation from equilibrium $\Delta P = P_0 - P$, which seems to be due to the increase in supercooling with the growth of ΔP.

Thus, the Topley–Smith effect for water evaporation when heat-feed was provided to the evaporation surface through the condensed phase was not observed at 20.5 °C. Note should also be made of the importance of taking into account, in kinetic measurements, the real conditions (temperature, pressure) in close proximity to the interface, which in the case of endothermal processes are certainly different from the thermostat temperature and the pressure measured in the system, which had been rightfully pointed out earlier, also in refs. 1–5. In this connection the presentation of the results of kinetic measurements in the form of curves v–P_{H_2O} at $T =$ constant, is also rather conventional since the real values of T and P_{H_2O} near the interface remain unknown.

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* The points of curves 2 and 3 correspond to average values for 5–6 experiments. The value of dispersion shown in Fig. 2 corresponds to the interval with a fiducial probability 0.9.

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