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NEW RESULTS ON THE DEPENDENCE OF THE LIQUID EVAPORATION RATE ON THE PRESSURE OF ITS VAPOUR

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ABSTRACT

The evaporation of water was carried out under various conditions of thermal contact of the liquid with the thermostat. This study especially shows how the various conditions of heat transport change the rate of evaporation particularly by the occurrence (or not) of the Smith—Topley effect.

INTRODUCTION

In a recent paper, Chupakhin and Lyakhov [1], referring to our work, have resumed the study of the dependence of the evaporation rate of water vs. the pressure of its vapour. Indeed, we have found that, in this case, the rate variation might show an unexpected feature expressed by a $v(P)_T$ curve with two extrema [2].

The results obtained from a thorough study of the phenomenon [2,3] resulted in the following interpretation: when an endothermic process occurs at an interface, accompanied by the elimination of a gas, the result is a large cooling of the interface and its environment. In addition, when the transport of calories occurs through thermal conduction in the gas the dependence of coefficient λ with pressure, under low pressure, results in the occurrence of the characteristic effect, i.e. the Smith—Topley effect mentioned above and common to evaporation, dehydrations, and drying of materials.

However, although the basic cause of this effect lies in the endothermic feature of the interface process of evaporation, the conditions of heat transport from the interface towards the reactor walls (number and nature of intermediates, for example) may change the external occurrence (magnitude, location of extrema in pressure and rate).

Following the paper cited [1], the new results reported below enable us to clarify the causes of disappearance of the effect and to specify the limits for the application of the Hertz—Knudsen—Langmuir formula.

EXPERIMENTAL

Procedure

The apparatus used is shown in Fig. 1. The "evaporator" (Fig. 1a) consists of a pyrex tube (ϕ = 30 mm) immersed in a thermostat whose temperature T_c is fixed.

The liquid to be evaporated was contained in a pyrex graded tube (ϕ = 12.5 mm); the height h of liquid, for all experiments, was about 10 mm. This tube was immersed in the gaseous phase and was supported to "the minimum".

The "condensed" part (Fig. 1b) was a metal vessel (ϕ = 30 mm, height 250 mm). The condensation surface consisted of the free surface of the liquid

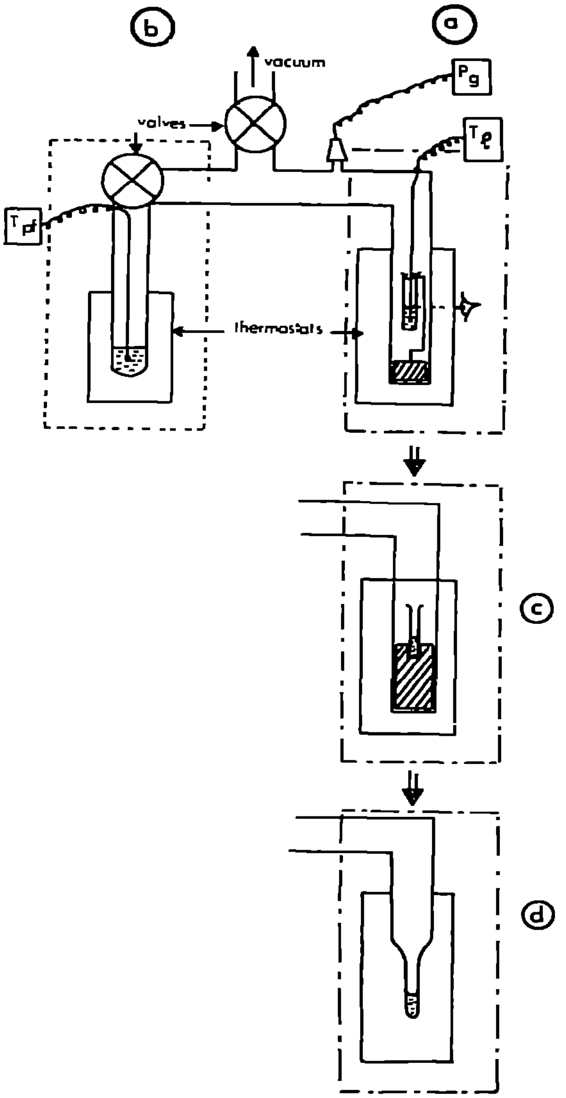

Fig. 1. Section of the evaporator—condenser. (a), (c) and (d) Evaporator section. Different assemblies used. (b) Condenser section.

and the vessel walls in direct contact with the thermostat; it was about 100 times larger than the evaporation surface.

The temperatures of the thermostats were set at about 0.2 degree. A system of valves allows the evacuation of the apparatus and the connection of both parts. A thin chromel—alumel thermocouple measured the temperature at different points. The interface displacement, due to the evaporation of the liquid, was observed using a cathetometer.

Figure 2 shows an experiment following simultaneously the variations vs. time of the temperatures T_{pf} (cold point) and T_{l} (liquid which evaporates), of the interface height Δh and of the pressure P at a given piont of the reactor.

The following points were established: (a) the cold point temperature remains almost constant, taking into account the setting; pressure is fixed in the reactor within a few seconds and remains constant; (b) the temperature of the liquid which evaporates first decreases rapidly for a few minutes, then decreases more slowly as it approaches the interface. A temperature profile is reported in Fig. 3; (c) the evaporation rate, the slope of the $\Delta h(t)$ curve, decreases from its initial value v_0 to v_{l}, reached when the temperature of the liquid becomes constant.

It should be noticed that the variation of v_0 vs. pressure does not exhibit any Smith—Topley effect [2]; alternatively, the $v_{\mathrm{l}}(P)$ curve can be characterised by this effect (curve in Fig. 4).

Chupakhin and Lyakhov [1] simultaneously brought two changes to the device described above:

(a) pressure was no longer fixed by a cold point but by an adjustable leak connected to vacuum;

(b) the tube containing the liquid was in direct contact with the thermostat.

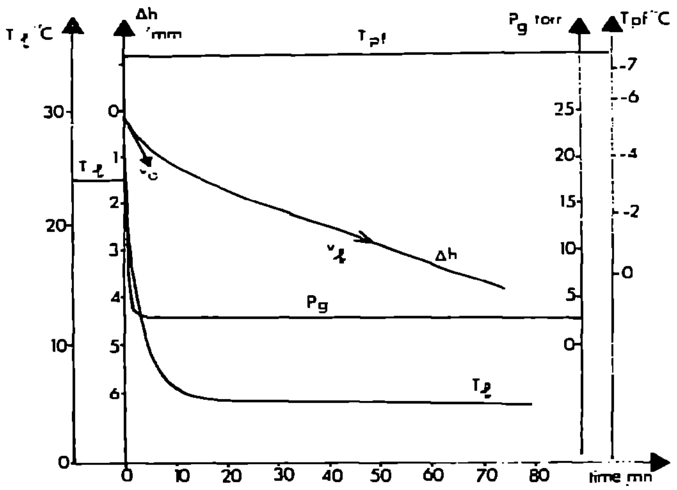

Fig. 2. Variation of different magnitudes of the system during an evaporation under T = 25°C and P = 2.5 torr. T_{pf}, temperature at a point of the cold point; T_{l}, temperature at a point of the evaporating liquid; Δh, height of evaporated liquid; P_{S}, pressure at a point of the gaseous phase.

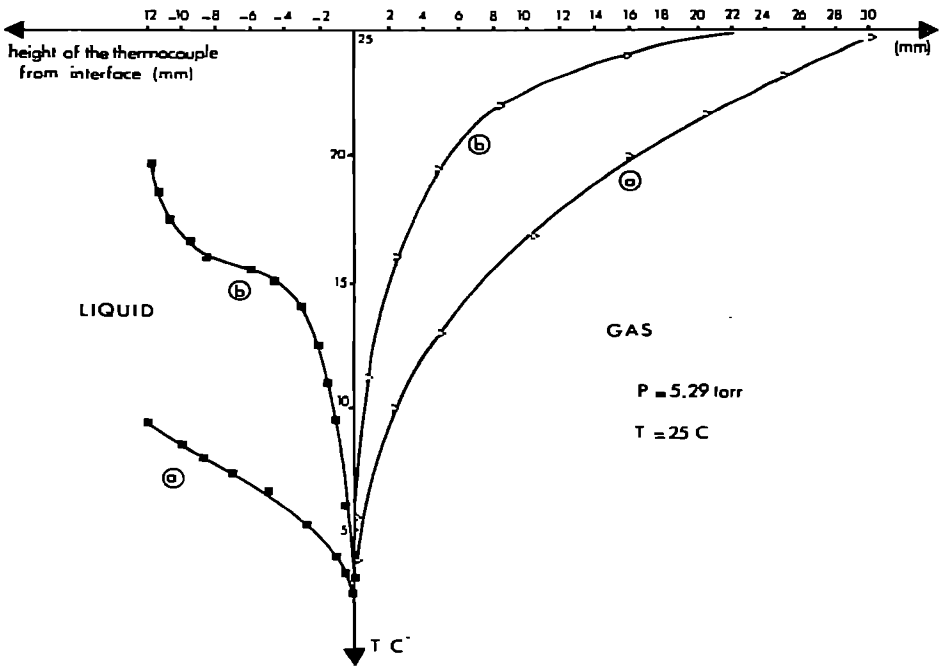

Fig. 3. Temperature profiles in the liquid and the gas during evaporation. (a) Assembly in Fig. 1(d); (b) assembly in Fig. 1(c).

In so doing they observed the disappearance of the Smith—Topley effect in conditions of temperature and pressure very similar to our experiments. But a priori the disappearance of the extrema on the $v(P)$ curve may be assigned to either change. This is why we chose to perform both operations successively.

Cold point or adjustable leak

First, the "condenser" part was replaced by an adjustable microleak so as to fix a constant pressure in the evaporator which is strictly identical.

The profile of the $\Delta h = f(t)$ curves remains unchanged; it is the same for the cooling of the liquid (Fig. 5). In addition, the evaporation rate v_l is not changed, as shown by the position of the isolated points Δ on curve (a) in Fig. 4. Therefore, the phenomenon of condensation cannot be expected to induce disturbing effects; both experimental procedures, microleak or condenser, appear as equivalent.

Thermal short circuit.

In a second phase, the contact was established between the thermostat and the tube using different materials (Fig. 1c); in the extreme case the tube containing the liquid to be evaporated was immersed in the thermostat (Fig. 1d). Compared to the previous case the $\Delta h(t)$ curves show, in all cases, a clear

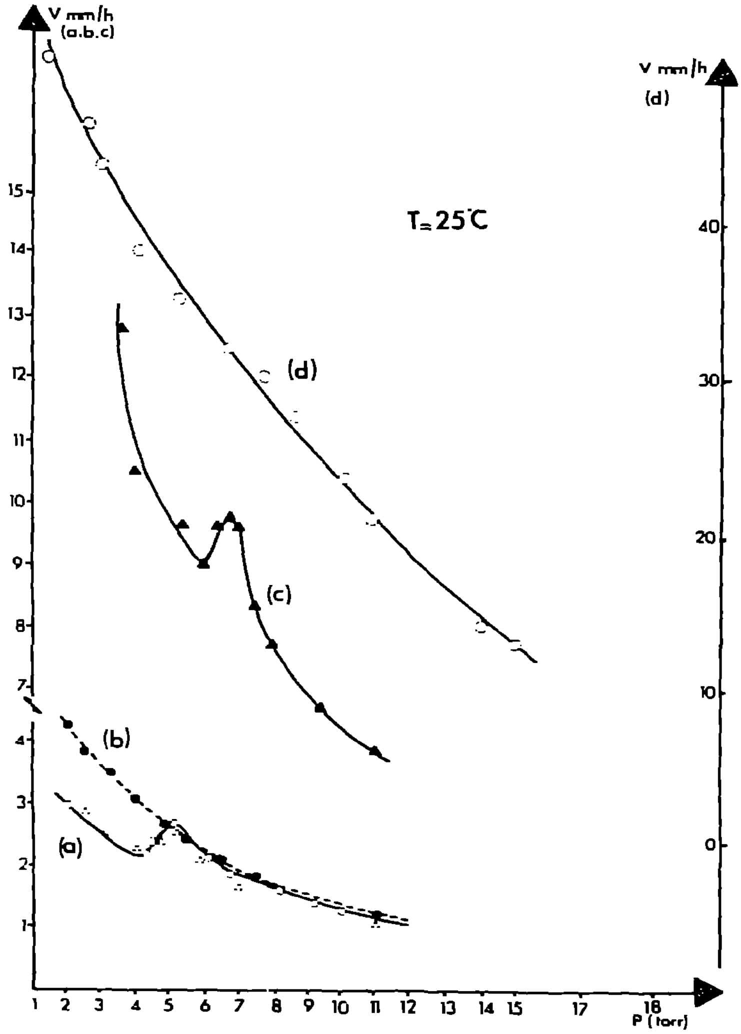

Fig. 4. Evaporation rate as a function of the pressure fixed at $T = 25°C$. (a) Assembly in Fig. 1(a): ○, cold point, △, microleak; (b) assembly in Fig. 1(c) — plexiglass contact; (c) assembly in Fig. 1(c) — duralumin contact; (d) assembly in Fig. 1(d).

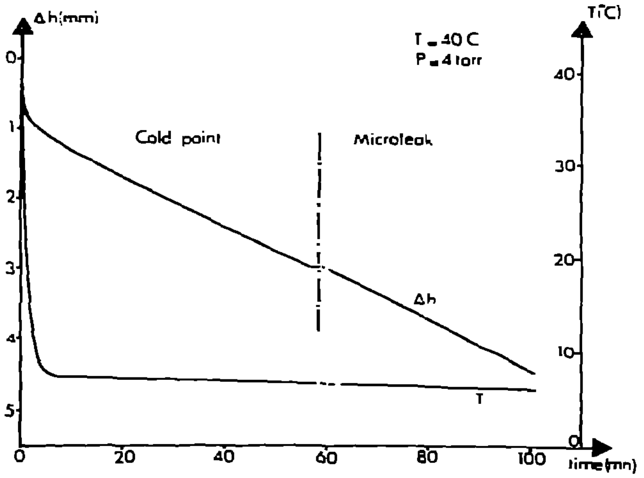

Fig. 5. Experiment carried out by fixing the same pressure successively by the cold point and the adjustable leak.

acceleration of the rate, and the set of measurements can be expressed as the pressure laws $v_1(P)$ of curves b, c and d in Fig. 4.

In the presence of a direct contact (Fig. 4d) between the thermostat and the interface, the result noticed in reference 1 is found again: the simultaneous disappearance of the effect with an appreciable increase in rate.

DISCUSSION

Disappearance of the Smith—Topley effect

This result is not surprising and confirms our interpretation, since by short-circuiting the transfer by thermal conduction in the gas the effect may disappear.

The efficiency of the contact between the interface and the thermostat will naturally change the external phenomena of the endothermic feature of the interface evaporation process. Using a plexiglass support we do not observe an important rate increase, only the Smith—Topley effect disappears (Fig. 4b). It will possibly occur again if a substantial increase in rate is obtained: this is the case with a duralumin support (Fig. 4c). Apparently the only direct contact of the thermostat with the liquid to be evaporated no longer allows this effect to be observed, at least at the temperature used here. The efficiency of the device in fact is not guaranteed over the whole temperature range. Also it does not seem to be ensured by the nature of the liquid to be evaporated.

Finally, it must be noticed that the absence of the Smith—Topley effect on the $v(P)$ curves does not prove that the problems of thermal transfer inherent to the state change have been solved, as shown in Figure 3. Whatever the material conditions of evaporation there is always a gradient in the gas or the liquid which evaporates, and we notice an increase in the interface gradients, especially marked on the liquid side, when the liquid is connected to the thermostat. In the latter case, the Smith—Topley effect disappears, but the problems of thermal transfer instead of being the rule occur not only in the gaseous phase but also in the liquid phase, so that the experimental evaporation rate cannot always be derived from the HKL relation.

Evaporation coefficient

The Hertz—Knudsen—Langmuir relation (HKL) [4] is often used as a basis for a quantitative description of the evaporation kinetics

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

(m = molecular weight, P = gas pressure, P_s = equilibrium pressure at a temperature T).

From this relation we may predict the variation of the evaporation rate with pressure. In the experiments mentioned above it is not so.

The parameter α contained in the HKL relation, termed evaporation coefficient, is in fact for controlled evaporation, a parameter allowing the adjustment of the calculated value of rate vs. its experimental value. A theoretical value of α should be known including all experimental data for the formula to have a role in prediction. Now, as recalled in ref. 1, α must be changed all along the $v(P)$ curve without any theoretical explanation of this $\alpha(P)$ variation and any prediction of the existence of the Smith—Topley effect on the $V(P)$ curves.

In addition, studies [5—7] show that, depending on transfer conditions, the values of α are largely different, despite the fact that the pressure and temperature in the reactor are maintained. Thus there is no reference value of α and hence of the experimental rate of evaporation for the evaporation of a given liquid.

CONCLUSION

Our overall study of which this paper is only a part [2,3], shows the importance of parameters — such as those which change the transport condition of heat towards the interface where the endothermic processes occur, the size of the heating vessels or also the extent of the reaction surface — in the value of the evaporation rate or magnitude or existence of the Smith—Topley effect.

With regard to the study of this effect, its possible disappearance by direct contact between the thermostat and the experimental vessel seems to prove our interpretation related to the dependence of this effect on the thermal conduction in the gas. But the disappearance of the extrema on the evaporation of a given liquid at a given temperature does not prove that this observation is general. In addition, it appears that the "normal" curve is still strongly dependent on the endothermic phenomenon whose importance varies with the distance to equilibrium. So far, no means used to neutralise this effect of endothermicity have been efficient enough.

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