Characteristic features of the evaporation of liquids

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Characteristic Features of the Evaporation of Liquids

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The evaporation rate variation of liquids (water, ethanol) is studied versus their vapour pressure. From measurements of liquid-vapour interface displacement versus time, the state change — whose rate is v_0 at initial time — is seen to slow down before reaching a constant rate v_1 under stationary working conditions. The difference between both rates increases as pressure decreases. In addition, whereas the $v_0(P)$ curves are monotonous and increasing from saturation vapour pressure to vacuum, the $v_1(P)$ curves have a typical shape, characterised by two extremums.

From the simultaneous measurement of temperature to assess the endothermic character of state change, it is shown that the previous observations may be related to the occurrence of a thermal flow at interface level.

The new profile of the $v_1(P)$ curves can neither be predicted nor explained from conventional expressions of evaporation rate. The present paper shows that a thermodynamic interface model involving coupling of mass and heat flows allows the features detected to be accounted for without any ambiguity.

INTRODUCTION

Examination of the literature devoted to the evaporation of liquids results in the idea that the experimental rate is always slower and sometimes even of a totally different order of magnitude than that derived from the Hertz–Knudsen theoretical expression.[1–6]

Several remarks, some of which have already been mentioned in previous studies, should be made after investigation of the reasons for this disagreement.

Theoretically, this expression of rate resulting from the kinetic theory of gases is obtained considering the reaction surface to remain at the temperature fixed although evaporation is endothermic.

From the experimental standpoint, several attempts have been made to reach an agreement between the phenomenon rate and that derived from

models, notably by trying to keep constant the interface temperature or by renewing the liquid surface[3-5] or by incorporating a heating surface in the liquid.[7] When the phenomenon was studied as such, i.e. when interface temperature was allowed to change most experiments were carried out in presence of extraneous gases and especially air: little work has been undertaken under low pressures. It, thus, seems that no work has been devoted to a systematic investigation of the pressure-temperature domain in a liquid-vapour phase diagram including the low-pressure domain.

Therefore, we resumed certain experiments trying to find out the features of evaporation in the simplest and best-defined conditions, i.e. when the liquid is in presence of its vapour alone, the value of the latter being controlled. Moreover, having found characteristic features of the dehydration rate versus pressure[8] (from a fraction to about 10 mm of Hg) we have decided to operate over this pressure range. Finally, we have reexamined the model of evaporation with the underlying idea that a law deduced from the thermo-dynamics of equilibrium states cannot account for kinetic results[4] and that it is essential to take into account the actual data of evolution especially the fact that it is endothermic.

APPARATUS AND OPERATING CONDITIONS

Figure 1 shows the evaporator-condensor. The "evaporator" part A consisting of a tube is immersed in a thermostat whose temperature T is that selected to cause evaporation. The liquid to evaporate is in a measuring glass tube separated from the rest by a support. The "condensor" part B, or cold point, is in a second thermostat and contains the same liquid. This cold point temperature determines the pressure, P in the reactor.
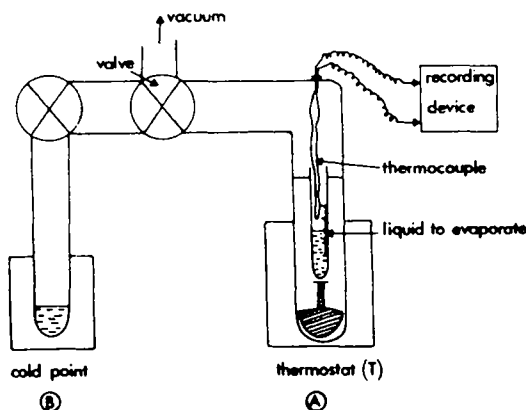

FIGURE I   Section of the evaporator-condensor.

To obviate the observations made in the evaporator being hindered by condensation, the condensation surface is about 100 times as large as that in the evaporator, the direct contact liquid-thermostat is achieved. The temperature in each thermostat is adjusted at 0.1 °C.

A valve system allows to evacuate, put into contact both parts of the apparatus and to admit a gas.

An experiment is carried as follows: About 3 cm^3 of the liquid to evaporate is put into the measuring tube. Both parts of the apparatus are evacuated. The system is allowed to recover temperature and pressure equilibrium. When equilibrium is attained the pressure in the evaporator is lowered by establishing contact with the cold point. The height of the liquid at $t = 0$ is the same in all experiments—it is 10 ± 0.5 mm—the liquid-gas interface displacement versus time is followed by means of a cathetometer: the temperature change is simultaneously recorded by means of a thermocouple.

The evaporation of water and ethanol, under the above conditions, led to the following results.

EXPERIMENTAL RESULTS

Interface displacement

A set of curves, showing the liquid height variation h versus time is listed in Figure 2. They are obtained for ethanol evaporation at a temperature of 27°C in the evaporator and under various vapour pressures.

The liquid level is noticed to lower very rapidly at the beginning, then following an intermediate period, it becomes linear versus time.

Under a very low pressure, such observations are no longer possible because the liquid boils.

Rate variation with pressure

The curves in Figure 2 show that two rates may be considered: the initial rate v_0 determined from the tangent slope at the origin of a curve $h(t)$ and rate v_1 in linear working conditions deduced from the slope of the $h(t)$ curves when they become straight lines.

Figure 3 shows the respective $v_0(P)$ and $v_1(P)$ plots for water and ethanol. The difference between both curves increases as pressure decreases, i.e. when the deviation from the equilibrium increases. In addition, whereas the $v_0(P)$ curves are monotonous and an increasing function from the liquid-vapour equilibrium pressure to vacuum the $v_1(P)$ curves are not and have a specific profile characterized by the presence of two extremums.
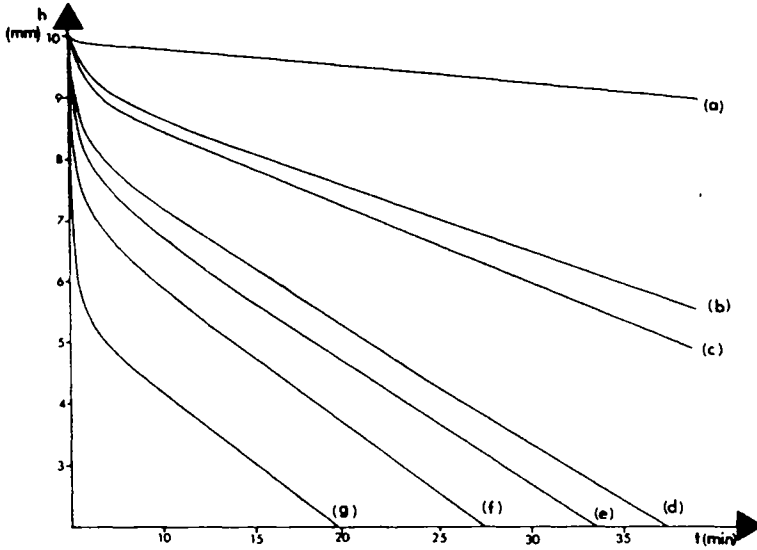
FIGURE 2 Ethanol evaporation. Set of curves $h(t)$ $T = 27°C$: a) $P = 49$ mm Hg; b) $P = 21.5$ mm Hg; c) $P = 15$ mm Hg; d) $P = 5$ mm Hg; e) $P = 4$ mm Hg; f) $P = 1.7$ mm Hg; g) $P = 1$ mm Hg.
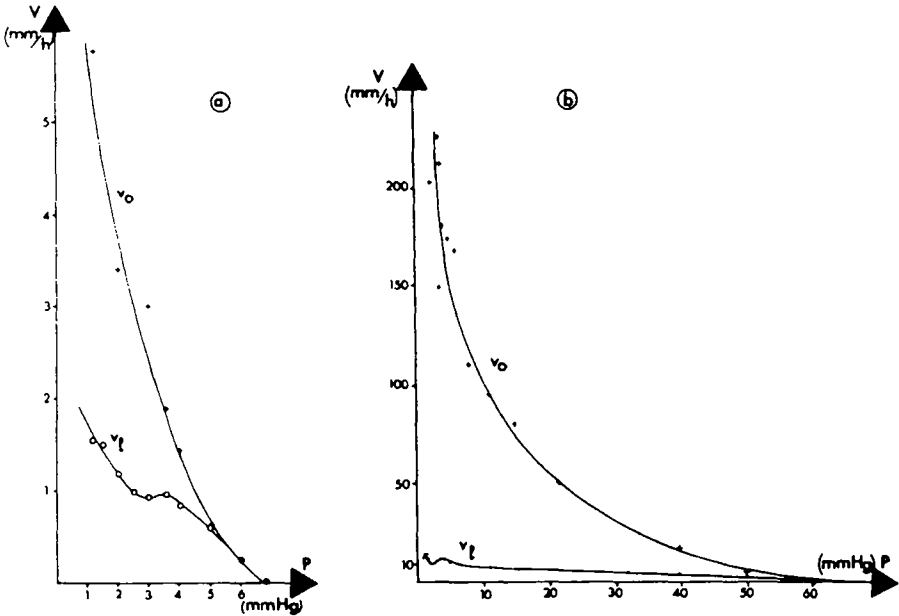
FIGURE 3 Evaporation rates v_0 and v_1 versus pressure; a) water evaporation $T = 5.5°C$; b) ethanol evaporation $T = 27°C$.
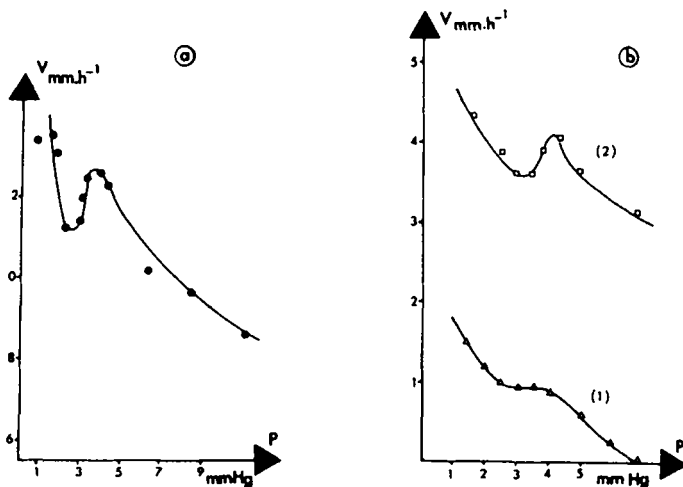
FIGURE 4 $v_1(P)$ pressure laws for liquids evaporation: a) ethanol evaporation $T = 27°C$; b) water evaporation (1) $T = 5.5°C$; (2) $T = 23°C$.

This unexpected feature of the $v(P)$ curves appears like a new element specific to the phenomenon of evaporation. Figure 4, which resumes and supplements Figure 3 with another scale shows this effect very distinctly.

Temperature change of the liquid over evaporation

As shown in Figure 5, the temperature of the whole liquid phase is noticed to fall sharply from the beginning, then to become and remain almost

FIGURE 5 Height variation and liquid temperature variation versus time. Ethanol evaporation $T = 27°C$; $P = 3.5$ mm Hg; a) curves (1) $h(t)$; (2) $T(t)$; b) curves (1) dh/dt; (2) dT/dt.

constant. The interface then moves at a constant rate v_1. Figure 5b shows the simultaneous interface temperature fall (roughly assimilated to t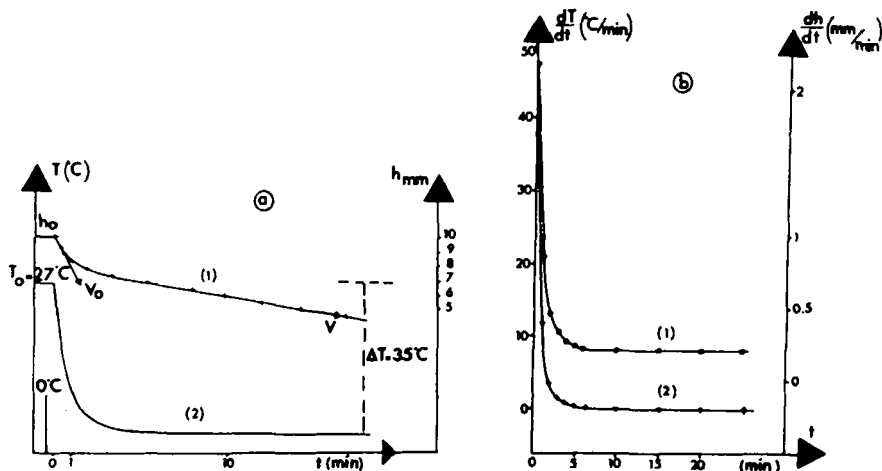hat of the liquid) and the evaporation flow fall from v_0 to v_1. In addition, a comparison of the ΔT values (difference between the thermostat and interface temperatures) obtained for various values of P (Figure 6) enables us to deduce the fact that the $v(P)$ curves plotted for a constant temperature of the thermostat, however, are not isotherms, since ΔT increases as pressure decreases.
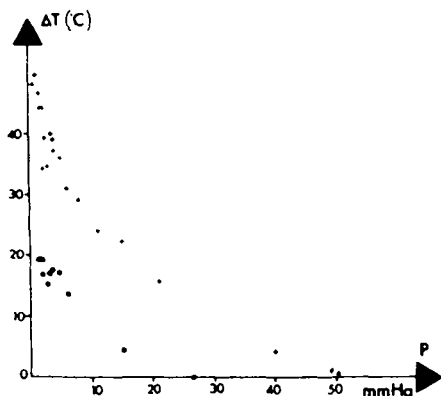
FIGURE 6 ΔT variation versus pressure, ● water evaporation $T = 23°C$: + ethanol evaporation $T = 27°C$.

DISCUSSION

The main features of the $v_1(P)$ plots showing extremums and the dependence of ΔT on pressure obviously result in the reexamination of the basis of the evaporation model, owing to the fact that previous interpretations, having neglected this difference, can only predict monotonous curves rising continuously from equilibrium pressure to vacuum.

Cause of the features observed

From the results obtained, it may be thought that the existence of a thermal flow generated by the endothermic character of the transformation is the cause of the effects observed.

The liquid-gas interface, which is the site of evaporation from the very onset, undergoes a very great thermal change. The thermal flow close to this interface is there to prove it. Moreover, as shown in Figure 5, the decrease of the evaporation rate from v_0 to v_1 is due to such a change. This is of major importance to interpret the $v(P)$ curves correctly.

v_0 which is the rate measured at initial time, thus when ΔT is zero, varies monotonously with pressure.

On the contrary, v_1 is the rate measured when stationary working conditions for mass and heat flow are established. The $v_1(P)$ curve shows two extremums and in this case the occurrence of a thermal flow is the cause of the effect observed.

Besides, the effect amplifier when the thermal flow becomes larger (e.g. by allowing the thermostat temperature to rise) is in agreement with this conclusion.

Hence it may be thought that if rate v_0 could be sufficiently slowed down for instance by allowing temperature to fall sufficiently or if the liquid investigated had a very low vaporisation heat, the $v_1(P)$ curve should not have any extremum.

Criticism of theoretical models usually used

For this purpose, two usual models of evaporation of liquids giving the rate versus vapour pressure at a given temperature will be analysed.

Let us first consider the Hertz–Knudsen relation

$$J_M = (P_S - P)(2\pi MRT)^{-1/2} \tag{1}$$

J_M is the evaporation rate, P_S the vapour pressure at temperature T and M the molar mass of the liquid.

This relation is deduced from the kinetic theory of gases assuming that the liquid-gas equilibrium is achieved at the interface.

Although this relation, obviously cannot apply to the evaporation which is the evolution of a system out of equilibrium[3-4] it has been frequently adapted to experimental results under given conditions, by means of an empirical coefficient α termed accomodation or evaporation coefficient. It is found in the Hertz–Knudsen–Langmuir relation.

$$J_M = \alpha(P_S - P)(2\pi MRT)^{-1/2} \tag{2}$$

The importance of α is shown by a few values in Table I precisely related to the evaporation of water.

TABLE I

Evaporation coefficient of water[5]

bulk liquid Temperature °C	Gas Pressure mm Hg	exposure time sec^{-1}	α
19.5	4.57	10^{-3}	0.198
4	2.69	10^{-3}	0.351
0	2.72	10^{-3}	0.415
0	0.76	10^{-3}	0.304

It is noticed that the difference between the calculated rate and the experimental rate (difference from α to unit) increases when pressure is lowered or temperature raised.

These conditions are those when the difference between v_0 and v_1 increases (Figure 3).

The second relation examined is that of Erikson.[9] It is a thermodynamic relation assuming isothermal conditions in the reactor, which comes to assume a thermal equilibrium during evolution.

$$\dot{n} = N_A^{-1} Ln(P_S/P) \qquad (3)$$

where n is the evaporation mass flow rate and N_A^{-1} is a temperature and equipment dependent coefficient.

This relation, thus, takes into account, at the interface, only the discontinuity of the chemical potential between liquid and gas. It, therefore, cannot predict phenomena due to other sources of irreversibility.

None of these expressions account for the phenomenon of evaporation correctly and the experimental results obtained allow the cause to be determined: the phenomenon of evaporation cannot be solely accounted for by the deviation to equilibrium for, from the very beginning, a thermal evolution occurs at the interface which becomes the site of a coupling between rate or mass flow and heat flow.

Establishment of an interface thermodynamic model

The underlying principle of such a model is to consider the liquid–vapour interface as a physical, material, two-dimensional medium characterised by a thermodynamic state and a site of generalised forces and flows.

In this case, the expressions of interface entropy production and interface entropic flow taking into account the irreversible phenomena at evaporation interface, may be written. Barrere and Prud'homme's[10] expressions in the general case of a mobile surface fit very well the problem of evaporation. Their equations were used by one of us to build up the model.[11] We shall recall here only the rate expression which can be attained in order to show that it allows the experimental features of evaporation to be found out.

$$v = -KrLn(P/P_S) + \frac{C_1 C_2}{\Lambda} rLn(P/P_S) - \frac{C_1 \lambda_0 G}{\Lambda}(1 - \exp(-P/\pi_0)) \quad (4)$$

where K, C_1, C_2, are phenomenological coefficients; C_1 and C_2 measure the coupling between both irreversible processes considered. G is the interfacial thermal gradient, λ_0 and π_0 characterize the gas thermal behaviour; P_S is the saturated equilibrium vapour pressure at interface temperature.
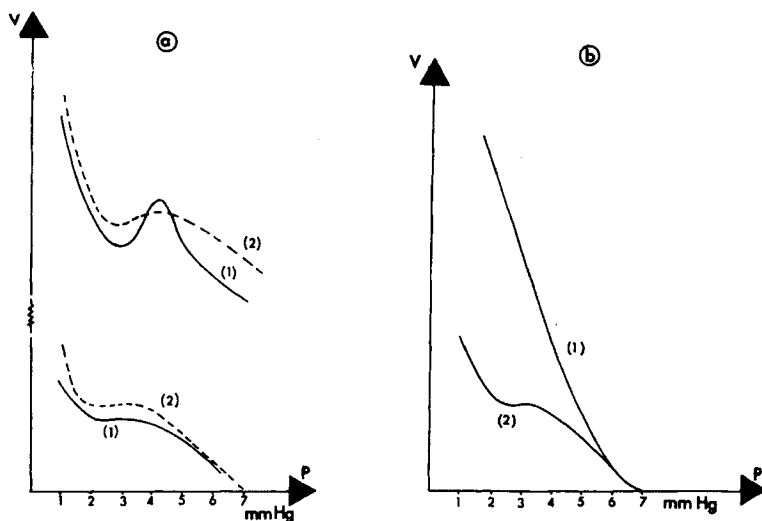
FIGURE 7 Comparison between model and experiment; a) water evaporation, (1) experimental curves (see Figure 4); (2) theoretical curves; b) Theoretical curves for water evaporation (may be compared with Figure 3); (1) curve plotted using the first term of expression (4) only; (2) curve plotted using the whole expression (4).

Figure 7 shows the comparison between model and experiment for water and alcohol. In each case, the $v(P)$ curve was plotted using an appropriate scale factor.

The plots in these figures show that the features experimentally observed are found qualitatively but without any ambiguity.

Firstly, as the experiment has made a distinction between initial rate and linear working conditions rate, the model distinguishes the curve plotted using the first term of expression (4) only (which takes into account, like of Erikson's,[9] the discontinuity of the chemical potential only) on the curve of (4) in which the second term involves coupling of the flows.

Secondly, the particular profile of the experimental $v_1(P)$ curve with its two extremums is also found using the model.

Finally, expression (4) allows a coefficient α assimilated to an evaporation to be defined. It is explained by the ratio of evaporation rates with or without thermal flow considerations.

$$E = 1 - C_1 C_2 / K\Lambda + \frac{C_1 \lambda G / \Lambda}{Kr Ln(P/P_S)} \qquad (5)$$

This coefficient tends towards unit if coupling and interface thermal gradient become negligible; in addition it varies with the evaporation

conditions. It should, however, be noticed that it is not the evaporation coefficient α which occurs in relation (2) itself derived from the kinetic theory of gases.

CONCLUSION

Experimental investigation of the evaporation rate of a liquid versus its vapour pressure allows certain characteristics to be put in evidence. One of them is the difference between initial rate v_0 and rate v_1 and the influence on the latter of displacement from equilibrium. The second is shown by a part, with negative slope, of the variation curve of v_1 with pressure.

As these features are not predicted by the usual relations of evaporation rate, we justify a model taking into account the irreversible phenomena of the interfacial medium and their coupling by the good qualitative agreement of the predictions yielded.

However, to make more progress in the knowledge of evaporation it is essential to come back to experiment and to use specific techniques of measurement of the main parameters of the interfacial medium and its environment, in particular interface thermal gradients, reaction front temperature and the variation of the coefficient of thermal conductivity with vapour pressure.

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