REVIEW

OPERATIVE REGIMES OF ACTIVE CENTERS AND THE GENERAL PICTURE OF
EFFERVESCENCE OF A LIQUID

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It is well known that boiling is the phase transformation of a liquid into vapor accompanied by formation of vapor bubbles in the liquid medium. The thermodynamic condition of commencement of boiling of a liquid (more accurately, the phase equilibrium of the liquid and the vapor) is that the chemical potentials of both phases are equal to one another:

$$\mu_\ell(p,\,T) = \mu_v(p,\,T).$$
(1)

From this condition it is in principle possible to determine the form of the phase equilibrium curve. This curve shows that the saturated-vapor pressure p_v is a monotonically increasing function of the temperature

$$p_v = f(T).$$
(2)

The relation (2) is equivalent to the dependence of the boiling point T_s on the external pressure p_0:

$$T_s = \varphi(p_0).$$
(2')

The curve of equilibrium of the liquid and vapor phases is limited below by the triple point and above by the critical point. This must be emphasized in connection with the recently widely circulated hypothesis of "pseudoboiling" of a liquid at supercritical pressures [1-3]. Since, according to Eq. (2), the saturated-vapor pressure p_{sat} cannot exceed the critical pressure p_{cr}, vapor bubbles cannot appear in a liquid under supercritical pressure and therefore it is impossible to talk about any type of boiling in this case.

Under ordinary conditions, as the liquid is monotonically heated (or the external pressure is lowered) there occurs a moment at which the vapor pressure p_v is greater than p_0. The chemical potential of the liquid phase μ_{sat} then exceeds the chemical potential of the vapor μ_v, and the liquid transforms into an unstable thermodynamic state, i.e., it tends to boil.

In this case, however, because of the potential barrier due to the surface energy the liquid may exist in a metastable, superheated state. Ya. I. Frenkel', following Gibbs, showed [4] that for a superheated or undercompressed liquid there exists a critical size of bubbles ("nuclei"), at which the size of the bubble will continue grow freely. The radius R^* of such a nucleus is given by the relation

$$R^* = \frac{2\sigma}{kT}\,\frac{V_\ell}{\ln(p_v/p_0)},$$
(3)

where σ is the surface tension and v_ℓ is the volume of the liquid per unit molecule.

The corresponding calculations and experiments show that for appreciable rates of bubble formation the vapor should be strongly supersaturated ($T \gg T_s$). But, as is now well known, under real conditions there always exist factors that significantly facilitate boiling. These factors are usually the active centers of boiling.

It was first shown in [5] that the most common type of active centers are pits (pores), containing very small bubbles of adsorbed gas, in the solid heating surface. This conclusion is now generally accepted. Nonetheless the mechanism of the bubble-forming action of such
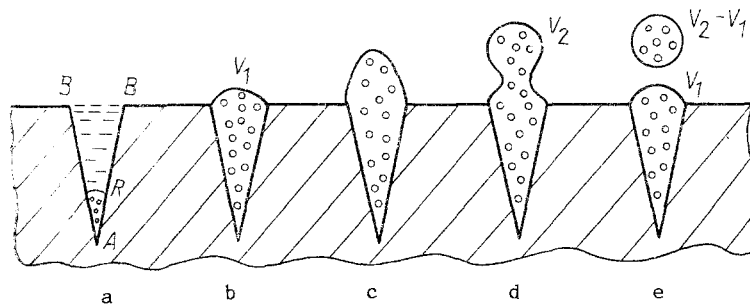
Fig. 1. Dynamics of a gas-vapor bubble in an active center under
conditions of effervescence.

pits and the effect of this mechanism on the thermophysical and hydrodynamic characteristics
of boiling as well as on the process of heat and mass transfer have still not been investi-
gated in detail. On the other hand, boiling is the most effective method for removing large
heat fluxes from high temperature surfaces and thereby makes it possible for modern techni-
cal installations to have high power capacity and reliability. For this reason the deter-
mination of the cause—effect relation between bubble formation and the heat transfer engen-
dered by it is an extremely important problem of thermophysics and thermal power engineering.

From the viewpoint of the kinetics of transformation of a liquid into vapor the initial
stage — effervescence — is of greaterst interest. In [5, 6], which are based on the experi-
ments of [7] and the theoretical ideas of [4], it was asserted that a liquid effervesces
not at protrusions of the surface of the heater, as was then believed [8, 9], but rather in
pits (pores) in the surface of the heater. It is the pores that are the main type of centers
which facilitate the appearance and subsequent growth of vapor bubbles. Other investigators
also subsequently arrived at the same conclusion [10, 11], and these ideas are now generally
accepted [12].

The next problem in the physics of boiling was to determine the mechanisms of the bub-
ble-forming action of the indicated centers and to construct a general picture of efferves-
cence of a liquid. At first we attempted to solve this problem by theoretical methods [13-
19]. We were able to obtain some important conclusions, but it gradually became clear that
this problem can be completely solved only by experimental study of the mechanisms of the
effect of the centers and the dynamics of the nonstationary temperature field in their
vicinity. This induced us to perform together with N. B. Chigarev the appropirate experi-
mental investigations. The experimental methods employed and the results obtained with their
help are described in [20-22].

In this paper we analyze theoretically and generalize the results of these investiga-
tions in order to obtain a general picture of effervescence of a liquid.

Let the temperature of the vessel together with the liquid contained in it increase
smoothly, as a result of heating of the bottom of the container with a constant heat flux
q = const, from room temperature up to the onset of developed bubble boiling. We shall
follow the molecular kinetic and hydrodynamic phenomena occurring as the liquid starts to
boil.

The surface of a real heater always contain narrow conical pits (pores), whose ver-
tices, as a rule, contain nuclei of the vapor phase — microscopic gas bubbles (Fig. 1a).
As the system is heated the temperatures of the different pits and adjacent liquid vary
in time in a complicated manner, forming around the center a nonstationary temperature
field.

The main idea of the experimental investigations [20-22] was to determine simultaneously
the dynamics of the nonstationary temperature field of an active center (with the help of
collection of microthermocouples) on the one hand and the characteristics of the bubble-for-
mation process occurring in it on the other (by the method of high-speed microfilling).
Such experiments were performed in a wide range of heat fluxes for different liquids and on
centers with different geometry.

Analysis of these experiments shows that prior to the onset of developed bubble boil-
ing three unique types of temperature fields and correspondingly three operative regimes of
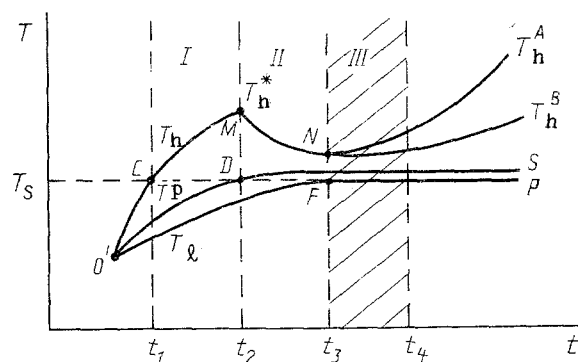
Fig. 2. Time dependence of the temperatures in a neighbor-
hood of an active center under the conditions of efferves-
cence: O'CMN is the temperature along the surface of the
pit T_h; T^P is the temperature of the liquid inside the cen-
ter; T_ℓ is the temperature of the liquid in the nucleus.

active vapor-formation centers are observed successively. Generalizing these facts, we can
say that the process of effervescence consists of three stages in time: I) preboiling, II)
underheated boiling, and III) boiling. The essence of each of these stages will be exam-
ined in detail below. For now, we note that, as follows from Fig. 2, stage I lasts from
the moment t_1, when the temperature of the surface of the heater reaches the value T_s, up to
the moment t_2, at which the temperature T^P of the two-phase medium within a pit becomes
equal to this temperature (during this stage the heater is heated from $T_h = T_s$ up to T_h^*);
the stage II continues from t_2 up to the moment t_3, when the temperature of the nucleus of
the liquid T_{liq} becomes equal to the saturation temperature $[T_{liq}(t_3) = T_s]$. The stage III
extends from t_3 up to t_4 — the onset of developed boiling. The duration of each stage is
determined by the heat flux q and the character of the size and shape distribution of the
active centers.

The dynamics of the temperature field near a center can be approximately described by
the time dependences of the temperatures of four points — the vertex A and the mouth B of the
pit T_h^A and T_h^B, the temperature T^P of the two-phase medium in the pore, and the temperature
T_ℓ of the nuclei of the liquid. Graphs of these functions are represented in Fig. 2, where
the dashed vertical lines at the abscissas t_1, t_2, t_3, and t_4 separate the region of efferves-
cence into the indicated stages.

We shall examine the thermophysical and hydrodynamic characteristics of each stage.

In stage I — preboiling — the temperature of the liquid not only in its nucleus but also
in the pit has still not reached T_s, so that no bubbles are released, and the center is in a
passive regime. However, because the temperature of the walls of the pore is increasing,
the mechanical equilibrium of the gas nucleus in it collapses — at first the bubble expands
rapidly, and then, because of adiabatic cooling, compression of the bubble starts. Ultimately
the gas bubble undergoes radial pulsations (in a number of cases it was possible to record
them by means of high-speed microfilming). The frequency ν of such pulsations in the case of
water is determined by Minnart's formula [23]: $\nu = 0.33/R$ kHz, where R is the height of the
conical bubble, in cm.

Since under real conditions the height R of the bubbles in the pores is of the order
of 0.22-0.1 cm, the frequency of their pulsations falls in the acoustic range. All this sug-
gests that the melodic "singing" of a preboiling liquid, well-known from practice, is the
result of acoustic emission by many elementary vibrators, pulsating in the pores of the gas-
vapor bubbles. With time the temperature of the heater increases, new centers are added to
the "singing chorus" of sound emitters, and the loudness of the acoustic accompaniment
increases. In the process, the height of the tone gradually decreases owing to the in-
crease of the size of the nuclei.

Preboiling is characterized by convective heat transfer with comparatively slow increase
of the heat-transfer coefficient α (Fig. 3).

The second stage — underheated boiling — is accompanied by sporadic detachment and re-
moval of gas-vapor bubbles from the active centers. These bubbles arise as a result of

evaporation of the liquid in the pore into the gas nucleus in the liquid. As a result the bubble starts to expand rapidly, pushing the liquid medium out of the pit. When it has reached the mouth of the pit, the gas-vapor cavity forms above it a dome stretching upward. There soon arises on it a tightening neck, along which the top part of the cavity detaches and floats up (see Figs. 1a-d). At this moment the mechanical equilibrium between the bubble remaining in the pore and the underheated liquid in contact with it collapses, since during the rapid (adiabatic) growth of the bubble in the pit the temperature and pressure of the bubble continuously decrease. For this reason, immediately after detachment the liquid once again flows into the pit the temperature and the pressure of the bubble continuously decrease. For this reason, immediately after detachment the liquid once again flows into the pit, compressing the bubbles to approximately their initial size (Fig. 1a, only the gas concentration it it has decreased). As our experiments showed, the compression cycle is significantly longer than the growth cycle ($\tau_2 \gg \tau_1$). In the compression process part of the vapor condenses and the temperature T^P increases, but there is not enough time for it to reach the value T_s. For this reason, when the entire cycle has been completed (the growth cycle plus the compression cycle) the center of boiling is in a passive regime for a long time $\tau \gg \tau_1 + \tau_2$, when macroscopic bubbles cannot form in it. During this "waiting" period the temperatures of the walls of the pore and the two-phase medium contained in the pore slowly increase.

Finally, when T^P becomes equal to T_s the center "comes alive" and the next cycle of bubble formation starts. Our measurements showed that, as a result of the repetition of such cycles the temperature T_h of the walls of the pore oscillates in time around an average value $\overline{T}_h$, which at first decreases rapidly and then more slowly (Fig. 2, the section MN). It can be said that during the stage II the centers operate in a nonstationary, pulsed state, and the intensity of heat transfer is appreciably higher than at the stage I.

By the moment t_3 the temperature of the nucleus of the liquid T_ℓ reaches the saturation point ($T_\ell = T_s$), and the liquid in the pore is somewhat overheated ($T^P > T_s$), so that the vapor bubble (there is now hardly any gas in it), which has grown from the center, is surrounded with saturated liquid. Since the vapor pressure in the pit is somewhat higher than the hydrostatic pressure p_0, the bubble in the pore grows freely and after being detached it is in a state of mechanical equilibrium. The liquid can no longer flow into the pore, the center starts to operate in a stationary manner, and the stage of true effervescence III, usually called commencement of boiling, starts.

The stage of commencement of boiling lasts for a finite time t_4-t_3, because the active centers do not enter simultaneously into the regime of stationary bubble formation because their geometries are different.

In the region III the vapor cavities, filling the pits, continuously grow from the minimum volume V_1 (see Fig. 1b) up to the maximum volume V_2 (Fig. 1d), when spherical bubbles of volume V_2-V_1 separate from them. The process then repeats, and the average temperature of the heater continues to increase and new centers, which are in a passive regime, are activated.

Designating the q-dependent time period of growth of the bubble from V_1 up to V_2 by τ^* (experiments show that $\tau^* \ll \tau$), we obtain for the rate of detachment in this stage the relation $f_{III} = 1/\tau^*$. It is obvious that the intensity of heating here is significantly higher than in the region II, where $f_{II} = 1/\tau$ (α_{III}, Fig. 3).

The graph, obtained from the experimental data and shown in Fig. 3, of the increase of the heat-transfer coefficient α as the liquid effervesces can be explained by the intensification of bubbling of the layer of liquid near the wall or intensification of the vapor-formation process.

Since bubbles are not released during preboiling, the weak growth of the coefficient α_I is obviously caused by the gradual increase of the pulsations (of the gas nuclei in the pits).

The coefficient α_{II} increases more rapidly at the stage of underheated effervescence ($\alpha_{II} > \alpha_I$). This is unlikely to be caused by vapor formation: After all, detachment of gas-vapor bubbles rarely occurs. There remains the conjecture that under conditions of nonstationary operation of the centers the sporadic oscillations of the vapor-gas cavity in the pit engender piston-like pressure pulses. These pulses give rise to more effective mixing of the close-lying layers of the liquid.
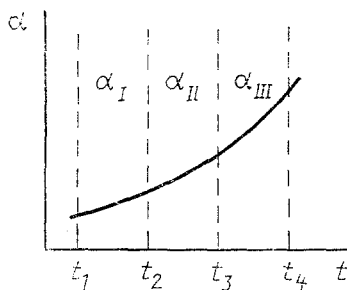
Fig. 3. Curve of the heat-transfer coefficient
$\alpha(t)$ at different stages of the process of ef-
fervescence.

Finally, when the liquid starts to boil, i.e., the stage III starts, the even faster
growth of the coefficient of heat transfer α_{III} is probably a consequence of the high rate
of detachment of bubbles, i.e., intense vapor formation.

It should be noted that the transition from the stage I to the stage II the character
of the acoustic emission changes from monopolar to dipolar, and unique changes also occur at
the transtion into the stage III. We examine this question in greater detail in a different
paper; here we only present the main conclusions.

The sound accompaniment of the second and third stages of effervescence, in contrast to
the melodic "singing" of the first stage, has the character of acoustic noise with a weak
maximum at a definite frequency ν_m. The intensity of this noise increases monotonically
from t_2 up to t_4, while the frequency ν_m, on the contrary, decreases smoothly [18]. Thus
the stage of effervescence can be judged from the character of the noise of the effervescing
liquid.

At the moment t_4 saturated boiling occurs in the system. This process is characterized
(for constant q) by a smooth decrease of the time interval τ^* and corresponding increase of
the bubble detachment rate f, i.e., the intensity of vapor formation. But no qualitative
changes appear in the mechanism of phase transformation of the liquid into vapor right up to
the onset of the crisis of boiling.

CONCLUSIONS

1. The process of effervescence of liquids consists of three successive stages with
different regimes of operation of active centers, intensities of heat transfer, and char-
acters of the temperature and acoustic fields.

2. The heat-transfer coefficient α increases continuously during the entire period of
effervescence, and at the boundaries of the stages its rate of growth increases abruptly,
i.e., $\dot{\alpha}_{III} > \dot{\alpha}_{II} > \dot{\alpha}_I$. The markedness of this effect depends directly on the magnitude of
the heat flux q.

3. The bubble-formation processes observed during the second and third stages of
effervescence are distinguished by the composition and detachment rate of the bubbles —
in the region II they are gas-vapor bubbles and in the region III they are purely vapor bub-
bles; the detachment rate f_{III} is more than an order of magnitude higher than f_{II}.

4. All stages of effervescence are accompanied by acoustic emission, but the character
of this emission (loudness, spectrum, timbre) differs significantly in them. This makes
it possible to employ the acoustic methods for remote control of the process of effervescence
and the intensity of heat transfer between the heater and the adjoining liquid.

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