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BOILING OF LIQUIDS

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IT is customarily assumed that boiling, i.e., intense vapor formation characterized by the production of vapor bubbles inside the liquid, has already been completely studied from the physical point of view. Consequently, far from sufficient attention has been paid to experimental and theoretical investigations of the kinetics of boiling of liquids. Only in the Thirties, when several new phenomena were observed in this field[1], did interest in the physics of boiling greatly increase. This was also stimulated by the fact that the liquid-vapor phase transformation processes are of great importance in heat engineering, metallurgy, chemical industry, nuclear power, and biology. In this article we review the last few years' research done on the physics of boiling.

1. HEAT EXCHANGE DURING BOILING. THE THREE STAGES OF BOILING

As noted by Bosworth[2], many investigators of the spheroidal state (the Leidenfrost phenomenon) have long ago expressed the idea that when the bottom and the walls of a vessel have a temperature much higher than the boiling point of the liquid in the vessel the boiling proceeds very slowly, and consequently the heat transfer is negligible. However, the question of the connection between the temperature of a solid surface and the rate of boiling (and the associated heat transfer) of a liquid in contact with it was not investigated at all for a long time.

Nukiyama in Japan[1] was the first to investigate, in 1934, the boiling of a liquid around a current-carrying platinum wire imbedded in it. Such a procedure enabled him to measure both the temperature of the wire and the rate of heat transfer from it. Even the first experiments with water have shown that with increasing current the wire temperature T increased continuously and smoothly to $T_1 = 150°$ C, at which instant, the water around the wire started to boil vigorously. Further gradual increase of the current did not raise the wire temperature. On the other hand, when the current became large enough, the temperature jumped suddenly to 1,000° C. With further increase in current, the temperature of the wire again increased smoothly, until the platinum began to melt. Similar results were obtained in experiments with wires of other metals and alloys.

Interesting results were obtained by Nukiyama also in the inverse process, that of cooling a platinum wire from 1500°C. With decreasing current, its temperature fell continuously, and with it the boiling rate, to 300°C. Further reduction in the current did not change the boiling rate, but the temperature dropped abruptly to a value somewhat higher than 100°C.

Nukiyama concluded from his experiments that the true dependence of the boiling rate v on the temperature drop $\Delta T = T - T_b$ between the superheated solid surface and the boiling liquid in contact with it has the form of the curve ABCE in Fig. 1. Section BC corresponds to unstable states and is usually not observed in practice. However, under certain conditions (for which the basic requirement is that the process be effected slowly) one can observe boiling corresponding to the transient process BC.

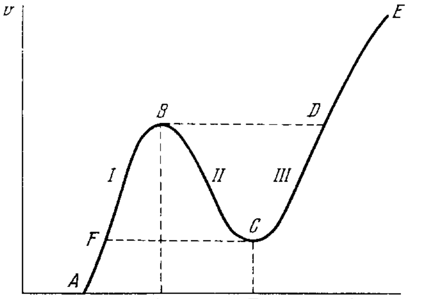

FIG. 1. Boiling rate v vs. temperature difference ΔT (between the heater and the boiling temperature of the liquid). T_0 – temperature of wire at the start of boiling; T_1 – first critical temperature, corresponding to the end of bubble boiling; T_2 – second critical temperature, observed when the heater is cooled at the instant of termination of film boiling.

Thus, if a copper bar heated to red heat is immersed in cold alcohol, boiling will occur on a clean hot surface reduced by copper-oxide vapor. With decreasing copper temperature, the rate of boiling of the alcohol, and with it also the rate of cooling of the bar, decreases; this corresponds to section EC in Fig. 1 (stage III).

When the copper temperature becomes equal to T_2 (point C), the boiling of the alcohol increases so much that the liquid usually splashes out of the vessel—this is section CB (stage II). The rapid increase in the boiling rate causes an extremely strong decrease in temperature, so that the system drops to the point B within a very short time interval. From this instant on, the rate of boiling again begins to decrease with cooling of the metal—this is boiling stage I (section BA). A similar picture is observed for incandescent silver immersed in water[3].

It must be noted that in this method of cooling, the better the surface finish and the cleaner the surface of the incandescent metal the more abrupt the boiling starting with point C.

Recently many investigations were made of the dependence of the heat transfer coefficient α (equal to the ratio of the heat flux q to the temperature differential ΔT) on ΔT, on q, on the surface-tension coefficient σ, on the type of liquid, and on the material and state of the solid surface.

Figure 2 shows the experimental $\alpha = f(\Delta T)$ curves obtained by Kutateladze and his co-workers[5], and also by McAdams[6], for water and liquid metal. In section I, α increases rapidly with increasing ΔT, in section II this coefficient decreases abruptly, and in section III it becomes practically constant.

The slope of section II depends on the degree of cleanliness and finish of the solid surface. Any contamination or roughness will cause the points of inflection of the curve to be somewhat different for different sections of the surface. The cleaner the surface, the steeper Section II of the $\alpha(T)$ curve. It is therefore natural to assume that a characteristic feature of this section is a discontinuity in the derivative of the heat transfer coefficient, $d\alpha/dt \rightarrow \infty$. Since the intensity of the heat transfer at a heater temperature close to T_1 (the so-called first critical point) is many times larger than during convection, boiling liquids have come into use recently as coolants.

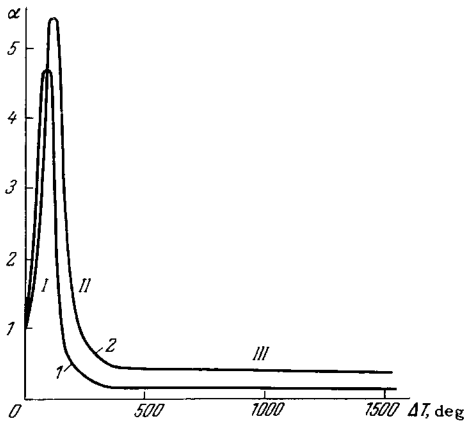

FIG. 2. Heat transfer coefficient vs. ΔT during boiling of water (1) and liquid metal (2). I – bubble boiling, II – transition, III – film boiling.

A typical plot of α against q is shown in Fig. 3. Section OA corresponds to boiling stage I, AB to II, and BC III.

As already shown by Nukiyama, the existence of three unique types of heat exchange in boiling is due to the existence of two different stages in the very process of the boiling of a liquid when the temperature of the solid surface is varied.

In the first stage the boiling is called nucleate or bubble; the vapor bubbles are produced at individual points of the hot surface of the solid—active centers. Various experiments, including photography, show that such an active center may be formed at any minute roughnesses, cracks, adsorbed particles, sharp ledges, boundaries between crystallites, etc.

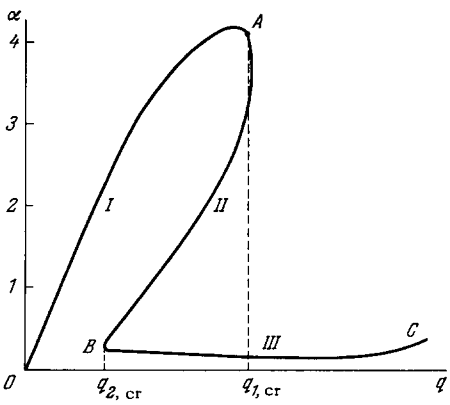

FIG. 3. The coefficient α vs. the heat flux q. q_{1cr} – heat flux corresponding to the first crisis; q_{2cr} – heat flux corresponding to the second crisis; OA – bubble boiling; AB – transition boiling; BC – film boiling.

With increasing temperature differential ΔT, the number of active centers increases, and the rate of boiling and heat transfer increase accordingly. The coefficient α reaches a maximum value when the entire solid surface is covered by such active centers. (The corresponding temperature differential ΔT_{cr} is called critical.)

With further increase in ΔT, coagulation of the bubbles sets in, and leads to formation of a solid film of vapor. This thin layer of vapor completely insulates the liquid thermally from the surface of the solid, convection ceases to play a noticeable role, and the value of the coefficient α decreases sharply. From this instant on, the vapor bubbles are no longer produced on the solid surface, but principally on the boundary between the liquid and the vapor. The rate of boiling becomes negligible. This is stage III—film boiling. Heat transfer in film boiling was investigated in detail by Kutateladze and his co-workers[5,15,16,28-30]. The film type of boiling was also investigated in [134,162-184]. The intermediate stage II, during which the produced bubbles on the surface of the heater coalesce, is called transition boiling. The mechanism of transition boiling is not yet clear. It was studied by many investigators, in recent years,[11,19,132-134,139,154-159,179,180] following Nukiyama, who could only establish the absolute instability of stage II. The indicated three types of boiling differ also in the intensity and the character of the accompanying acoustic noise. Osborne and Holland[31] noted that when the temperature differential ΔT increases the loudness of the sound in the region of bubble boiling increased from 2 to 18 db; during the time of transition boiling, it reached 26 dB, remaining practically constant after the start of film boiling. Characteristic differences are observed also in the sound spectrum of the noise of each type of boiling. We now proceed to consider the conditions under which the transition from bubble boiling to film boiling occurs.

In this respect, interesting results were obtained by Kutateladze et al.[15-17] on the connection between a heated wetted surface and the temperature at which film boiling sets in. The poorer the wetting of the surface by the liquid, the earlier film boiling begins. If the contact (wetting) angle is close to 180° (zero wetting), stable film boiling occurs at small temperature drops ΔT. Thus, the greatest boiling rate can be attained with total wetting, when the coagulation of the bubbles is made most difficult. During the inverse process, when the temperature drops from film to bubble boiling, the transition point T_{2cr} lies lower than in the direct process of rising temperature. This is the so-called second critical temperature, distinguished from the first, T_{1cr}, at which the transition from bubble boiling to film boiling takes place. In other words, on going from bubble boiling to film boiling a characteristic hysteresis is observed, which is apparently connected with the presence of some surface potential barrier. The practically important question of the critical values of the heat flux q_{1cr} and q_{2cr} and their dependence on the external pressure was also investigated by Kutateladze and his co-workers[5]. They have established that usually the critical points are quite pronounced on the $\alpha = f(q)$ curve. Only in individual cases, in the case of small and smooth variation of the heat flux q, is it possible to observe "supercritical" states. At heat-flux densities between the two critical values, $q_{2cr} < q < q_{1cr}$ it is possible to realize both bubble and film boiling.

Based on the assumption that the transition from bubble boiling to film boiling is a hydrodynamic rearrangement of the boundary layer, Kutateladze obtained with the aid of similarity theory the following relations for the first critical heat flux:

$$q_{1\,\mathrm{cr}} = \mathrm{const}\cdot\lambda\sqrt{g\varrho'}\,\sqrt[4]{\sigma(\varrho-\varrho')}.$$

This formula agrees well with the experimental data of Kazakova[24], Farber and Scorah[25], Braunlich[6], and Aikin and McAdams[26] for water, and the results of Cichelli and Bonilla[27] for organic liquids. Analogous formulas were obtained by G. N. Kruzhilin, V. A. Tolubinskiĭ, and I. I. Novikov.

From general theoretical considerations, Kutateladze deduced[5] that the ratio of the critical heat fluxes q_{2cr}/q_{1cr} for a given liquid is a constant quantity, always smaller than unity. Experiments have confirmed this.

A thermodynamic theory of the changes in the character of boiling was recently developed by V. P. Skripov[215]. According to this theory both critical temperatures T_{1cr} and T_{2cr} (and accordingly q_{1cr} and q_{2cr}) correspond to the start and finish of a single boiling "crisis." The hysteresis on the curve is a consequence of the ambiguity of this function. To the contrary, the character of the heat transfer is completely determined by the surface temperature of the heater.

Skripov's main idea is that the boiling "crisis" is a thermodynamic crisis. The thin layer of liquid adjacent to the heating surface is in a superheated state. This metastable layer may turn out to be underheated with respect to a microscopic bubble produced inside it. With increasing surface temperature, the temperature of the boundary layer will also increase, until the superheat limit is reached.

From this instant on, contact between the liquid and the heater, becomes impossible even for small time intervals, and film boiling sets in. Transition boiling, according to Skripov, corresponds to a mixed mode with spatial and temporal alternation of bubble and film boiling. The correctness of these premises was confirmed by the experiments of Skripov and his co-workers, who have shown that T_{2cr} is close to the temperature of the superheat limit of the corresponding liquids.

In addition to the three main types of boiling considered above, there are other particular types of boiling, characterized by certain singularities. These include boiling in a moving liquid. This type of boiling, which is of great importance for modern heat power engineering, was investigated in detail at the Central Turbine and Boiler Institute[18-23,139,140,148], and also by the authors of[131,146,181]. They investigated for the most part the dependence of the heat transfer on the velocity and character of motion of the boiling liquid. The laws governing the growth of vapor bubbles in a moving liquid were analyzed by V. K. Zavoĭskiĭ[216].

Another particular case is local or unsaturated boiling. It is observed when the liquid is at a temperature below the boiling point T_b but the solid surface of the heater has a temperature $T > T_b$. In local boiling, bubbles are produced on the hot surface, break away, grow in size, fall into colder layers of liquid after reaching a certain size, are compressed by these layers, and vanish. The practical significance of local boiling lies in the fact that the heat transfer is much larger in this case than in convection. Therefore in some high-temperature processes (quenching of metals, cooling of the metallic structures of furnaces and reactors, etc.) large amounts of heat can be removed by using liquids underheated below T_b. The dependence of the rate of local boiling on the temperature differential ΔT is in general outline similar to the same dependence for ordinary boiling. Local boiling is dealt with in many papers[32,33,185,217].

2. EXPERIMENTAL METHODS OF INVESTIGATION OF BOILING

The physical process of boiling is being experimentally studied by two direct methods—high speed photography and analysis of the acoustic noise.

a) The photographic method came into extensive use during the last 25 years and is continuously being improved, primarily by reducing the exposure time. Thus, Westwater[7] and Santangelo, using an exposure of 10^{-6} sec, succeeded in 1955 in obtaining a tremendous number of instantaneous photographs of the entire boiling curve.

At the same time, researchers started to use motion picture photography, which made it possible to trace the dynamics of the process. However, the usual speed of 16 frames per second, first employed for this purpose, produced pictures that were too blurred. Higher speeds of 64 and 200, and then 500 frames per second were subsequently adopted[7,11]. At these speeds, the pictures still remain blurred to a considerable degree, thus indicating the high speed at which the process takes place. In 1948, Dew used a speed of 2,000 frames per second, and a few years later Westwater and Santangelo went to 4,000 frames per second, and Gunther even to 20,000 frames per second. Even higher speeds were successively used for a small number of photographs[34,35].

High-speed motion picture photography was used, in particular, to investigate the formation of bubbles in volume boiling, the collapse of bubbles during the instant of the emergence from the liquid, and other phenomena. The main use of this method, however, was to study bubble boiling[36,37,98,241]. For example, the rate of detachment of the bubble from the active center on the hot surface was determined, and found to fluctuate in these experiments between 15 and 20 bubbles per second. The dimensions V of the bubbles at the instant of detachment ranged from 2.5 to 5 mm. The photographs show clearly the active centers on the surface, between which an area free of bubbles is found. A photograph of boiling for the critical temperature difference, at which the entire surface is covered with the active centers, was obtained. The same method (frequency 15,000 sec^{-1}) was used by G. G. Treshchev[131] to investigate boiling in a moving stream.

b) Boiling noise. The character of the boiling exerts a noticeable influence on the acoustic noise accompanying this process. Osborne[38] measured the dependence of the intensity of the integral boiling noise on ΔT in the interval from 25 to 7500 cps. Figure 4 shows a plot of this dependence, from which it is seen that the sound intensity I increases on going from bubble boiling to film boiling. The sound intensity depends strongly on the degree of degasification of the liquid. Osborne used in his measurements a hydrophone as a sound receiver (pickup). When placed under water, this hydrophone transformed the mechanical oscillations and the pulsations produced by boiling on a hot wire into electrical signals. The latter were analyzed with the aid of an electronic receiver and amplifier. The procedure for measuring the noise of a boiling liquid was subsequently expanded and perfected. Although in principle various methods of acoustic measurements in liquids have been developed in sufficient detail[39,40], we have here many specific peculiarities.

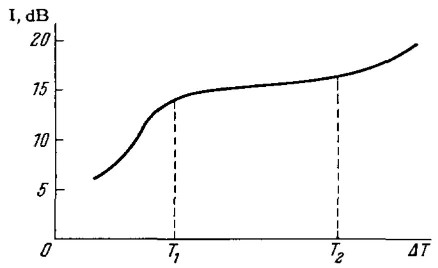

FIG. 4. Dependence of the boiling-noise intensity I on the temperature differential $\Delta T = T - T_b$. T_1 - first critical temperature, T_2 - second critical temperature.

The acoustic intensity is determined by measuring some quantity connected with the amplitude of the sound wave.

There are several different methods of intensity measurement: 1) mechanical, 2) optical, 3) calorimetric, 4) piezoelectric. The latter is based on measurement of the amplitude of the sound pressure with subsequent recalculation to intensity. The piezoelectric method is the most frequently used in practice.[41,42]

Figure 5 shows a block diagram of one of the instruments for intensity measurements. This instrument consists of three fundamental units: a receiving section (pickup) (1), an amplifier (3), and a recording section (vacuum tube voltmeter) (4). The piezoelectric pickup (1) (most frequently made of barium titanate) is placed in the working vessel (2), in which ultrasonic oscillations are excited. The voltage developed by the pickup is amplified by amplifier (3) and is measured with the vacuum tube voltmeter (4).

We note that the piezoelectric probe must have a high frequency-independent sensitivity. In addition, it must not have a pronounced directivity.

In addition to the two indicated direct methods, an indirect thermal method is extensively used for experimental investigations of boiling, in which the thermal and temperature conditions on the boiling surface are determined. This method has been used most frequently to investigate boiling on an electrically heated horizontal platinum wire. The heat flux

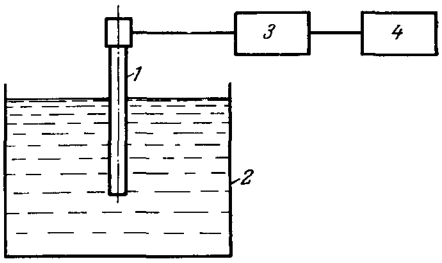

FIG. 5. Block diagram of setup for the measurement of the intensity of boiling noise.

can then be calculated from the electricity consumed and from the surface area of the wire. The temperature differential ΔT is measured by the thermoresistance method and by introducing a suitable correction for the radial temperature gradient in the wire[6].

3. HEAT TRANSFER THEORIES

One of the most important theoretical problems of the physics of boiling is the derivation of the functional dependence of the heat transfer coefficient α on the conditions of the process. At present there is no theory at all for heat transfer in transition boiling. For film boiling, the first steps in this direction were made in [183,184], but the problem is still far from solved.

More theoretical research has been done on heat transfer in bubble boiling. Many different theories have been developed, and this is also evidence of the unsatisfactory state of the question. The difficulty in deriving a formula for the coefficient α is due primarily to the dependence of this quantity on a large number of various factors, as already mentioned in Sec. 1. Experiments show that the heat transfer increases[5] with increasing external pressure P_0, and decreases[129] with decreasing P_0. The value of the coefficient α depends on the duration of the boiling on the given heating surface. Immediately after the liquid begins to boil, α can be considerably higher than after prolonged boiling. The reason is obviously that the unstable boiling centers have been removed during the initial state of the process (decrease in the number of ready gas bubbles filling the pores in the solid surface, etc.).

The coefficient α depends also on the viscosity of the liquid. According to experiment by V. I. Tolubinskiĭ[5]

$$\alpha \sim \nu^{-0,3}$$

(ν is the kinematic viscosity). In bubble boiling there is also a direct connection between the heat transfer coefficient α and the heat flux q, namely the empirical formula

$$\alpha = \mathrm{const} \cdot P_0^{0.4} q^{0.7} .$$

For a given heat flux q the intensity of the heat transfer depends not only on the temperature differential ΔT, but also on the absolute values of the heater and liquid temperatures. In addition, the value of α is influenced by the dimension, shape, and position of the heater surface, the character of its prior mechanical and physico-chemical finishing, and the cleanliness of the boiling liquid[246].

In spite of the indicated difficulties, several theories were advanced for heat transfer in bubble boiling. One of them is due to Rohsenow[8]. His basic assumption is that heat is transferred from the hot surface directly to the interior of the liquid, and from the latter to the vapor bubbles. The decisive factor for the heat-exchange intensity is in this case the character of motion of the bubble immediately after the detachment from the solid surface, since the detached bubble causes intense bubbling of the surrounding liquid and improves the convection. Inasmuch as the heat transfer from the solid to the liquid is characterized by the dimensionless Nusselt number $\mathrm{Nu} = \alpha l/k$ (k—heat conduction coefficient of the liquid), which is a function of the Reynolds and Prandtl numbers, $\mathrm{Nu} = f(\mathrm{Re}, \mathrm{Pr})$, the problem reduces to finding the form of the unknown function f, determined by the character of the convective motion of the liquid. Rohsenow proposes the following equation

$$\mathrm{Nu} = c\,(\mathrm{Re})^a\,(\mathrm{Pr})^b, \qquad (*)$$

where a, b, and c are constants for a given type of motion. From empirical considerations, Rohsenow assumes that $a = 2/3$ and $b = -0.7$. The Reynolds number $\mathrm{Re} = \rho v l/\eta$ must be defined, in accordance with this theory, for the just-detached bubble. To find its diameter D, which characterizes the linear dimensions l of the moving body, Rohsenow uses the well known formula[5]

$$D = \mathrm{const} \cdot \theta \sqrt{\frac{\sigma}{\varrho - \varrho'}} ,$$

where θ is the wetting angle and ρ' the vapor density.

As applied to boiling, Rohsenow defines the velocity v as the amount of vapor produced on a surface of 1 cm^2 area per second.

Obtaining in this manner the value of the Reynolds number, Rohsenow substitutes it together with the Prandtl number into the equation $\mathrm{Nu} = c(\mathrm{Re})^a(\mathrm{Pr})^b$ and arrives at the relation

$$\alpha = \mathrm{const} \cdot (\Delta T)^2 ,$$

where the constant does not depend on the parameters of the liquid or the solid. Forster and Zuber reason somewhat differently[7,9]. They take as their starting point the Rayleigh equation (which will be discussed in detail later) for the radius of the bubble inside the liquid

$$RR'' + \frac{3}{2} R'^2 + \frac{2\sigma}{\varrho R} = \frac{P - P_\infty}{\varrho} .$$

Adding to it the relation obtained by Zuber et al. (see [7]) for the heat transfer on a spherical surface, and taking into account the dependence of the saturated vapor pressure on the temperature, they obtained for the speed of motion of the bubble walls the following differential equation

$$\frac{dR}{dt} = \mathrm{const} \cdot \frac{\Delta T}{\varrho \sqrt{t}} ,$$

where ΔT is the temperature difference between the liquid and the vapor, t the time, and ρ' the vapor density. The constant on the right side of the equation depends on the type of liquid and is expressed in terms of the characteristic quantities (specific heat, thermal conductivity, density, etc.). Thus, the product $RR' = \text{const} \cdot (\Delta T/\rho)^2$ does not depend on the time (i.e., small bubbles increase rapidly, and large ones slowly).

Knowing RR′, Forster and Zuber determined the Reynolds number $\mathrm{Re} = RR'\rho/\eta$ for a bubble rising to the surface, and then, like Rohsenow, obtained the connection between the Nusselt number Nu and the Reynolds and the Prandtl numbers in the form (*). As a result they obtained a rather cumbersome formula relating the heat transfer coefficient with the temperature drop and with the parameters of the liquid. It is noted in the review[7] that the Forster-Zuber formula agrees better with experiment than the Rohsenow formula. As can be seen from the foregoing, Forster and Zuber's conception is that the heat transfer during boiling is a consequence of a continuous evaporation of liquid into the bubble during the time that it floats upward. A similar idea was advanced also by Zwick[7], who attempted to simplify the Forster-Zuber formula.

The Soviet school of heat-power engineers is analyzing the process of heat transfer during boiling in greater depth. G. N. Kruzhilin[13] considered the nucleation and motion of individual bubbles in a superheated liquid. The radius of curvature of the smallest roughness projection that can serve as a vapor-formation center is equal to

$$R_0 = \frac{2\sigma}{\Delta P} = \frac{2\sigma}{P'\Delta T}.$$

Here ΔT is the superheat and $P' = dP/dT$ a quantity determined from the Clapeyron-Clausius equation. With increasing superheat ΔT, the minimum radius R_0 decreases and the number of vapor-formation centers increases accordingly, and with it the heat transfer coefficient α. Starting from these notions, Kruzhilin obtained a criterial formula for heat transfer during boiling.

A different path was followed by S. S. Kutateladze and his co-workers[5,10-12] (and also by A. S. Éigenson; see [138]). From the complete system of equations describing the motion of the liquid and the vapor phases and the conditions for the formation and detachment of bubbles, Kutateladze obtained several primary and derived similarity criteria. He then expressed α in the form of an implicit function of the similarity-criteria parameters. To obtain a formula that can be conveniently checked by experiment, Kutateladze discarded secondary criteria and confined himself to the numbers Re and Pr.

A distinguishing feature of Kutateladze's method is the separate and independent analysis of the processes occurring in the liquid and vapor phases. This model is combined into a single entity by means of the boundary conditions, which coincide for both systems.

A. A. Gukhman's co-workers L. S. Sterman and N. G. Styushin[136-138] solved the problem of the heat transfer during boiling by considering a single system of equations for both phases. Somewhat different formulas were obtained by the Kiev researchers M. A. Kichigin, N. Yu. Tobilevich[14], and V. I. Tolubinskiĭ[175]. There exist also other formulas of the same type[3,4,139-153,178,226,227]. Each theory is based on a different initial process, but all the authors derive their equations by the methods of similarity theory. Therefore semi-empirical heat transfer formulas of this kind are essentially equivalent. Recently D. A. Labuntsov[218] developed a new physical theory of heat transfer during bubble boiling. This theory takes account of the fact that the vapor bubbles are produced only at individual points of the heater surface—active centers. These are usually pores, cracks, scratches, and the like, and are areas with lower wettability. With increasing temperature differential ΔT, an increasing number of rough spots turn into real boiling centers. It follows from very general considerations that the number of active centers n is proportional to the square of the superheat.

$$n = \text{const} \cdot \left(\frac{\lambda\varrho'\Delta T}{\sigma T_c}\right)^2.$$

Labuntsov further assumes that the evaporation of the liquid occurs principally at the base of the produced bubble. The heat consumed in evaporation is drawn from the heater by thermal conduction through the layer of liquid adjacent to the interface between the solid and the vapor.

Assuming that the growth rate of sufficiently large bubbles is determined under isobaric conditions by the intensity of the heat supply,

$$\lambda\varrho' \frac{dV}{dt} = \int\limits_S q\, dS,$$

Labuntsov obtained for the bubble radius R the relation

$$R = \text{const} \cdot \sqrt{\frac{\Delta T}{\varrho'} t}.$$

This formula differs from that employed by Forster and Zuber in the presence of the square root sign in front of $\Delta T/\rho'$.

One more assumption is made in this theory. Although the nucleation, growth, and detachment of the bubbles in the liquid volume gives rise to intensive bubbling, at the very surface of the heater the liquid (between the bubbles) is stationary. Starting from the foregoing considerations, Labuntsov obtained a formula for the total heat flux density q, which consists of the heat flux q_1 via thermal conduction through the stationary layer of liquid, and the flux q_2 going into evaporation:

$$q = A\,[(\Delta T)^3 + B\,(\Delta T)^2],$$

where A and B are certain parameters that depend on the properties of the liquid and of the solid surface of the heater. This formula agrees satisfactorily with results of experiments on the boiling of water, benzene, ammonia, and other liquids [219-223]. It follows from Labuntsov's formula that the external force fields should not influence the laws governing the heat transfer during bubble boiling. This agrees with experiments performed under conditions of inertial overloads [224] and under reduced gravitational forces [225].

According to the theory developed by the author of [147], the coefficient α consists of two terms: α_1, which characterizes heat transfer via vapor production, and α_2—via bubbling. For boiling on a thin wire or boiling of a very viscous liquid, $\alpha_2 \approx 0$ and $\alpha = \alpha_1$, and the dependence of α_1 on the conditions of the process takes the form

$$\alpha_1 = A\,(\Delta T)^2\,\lambda\,\frac{dR}{dT},$$

where the constant A depends on the state of the heater surface.

4. FORMATION OF BUBBLES. CRITICAL NUCLEUS

It has been long known in physics that although the transformation of matter from the liquid into the gaseous state occurs both by boiling and by evaporation, the former is much more complicated than the latter. This is evidenced first of all by the fact that boiling of a liquid begins usually at a definite temperature that depends on the external pressure. It was observed already at the end of the 18th century that the boiling point depends on the material of the vessel; the better the liquid wets the walls of the vessel, the higher the boiling point. At approximately the same time it was noted that the dissolved air has an influence on the boiling temperature of water, and that thoroughly degassed water at normal pressure can be raised to about 200° C before it begins to boil. In 1861 it was even stated that a perfectly pure liquid, containing no dissolved gases, cannot boil at all [43].

The first major contribution to the theory of the boiling process was the research carried out by W. Gibbs [44] on the conditions of heterogeneous equilibrium. Gibbs explained first why superheating of a liquid is possible. A liquid stay in a relatively steady metastable superheated state because the system must overcome a certain activation barrier before it can go over into a stable vaporlike state. The existence of this barrier is connected with the fact that when a bubble is produced in a superheated liquid, the thermodynamic potential decreases, on the one hand, because the molecules go over into a more stable state (volume effect), and increases, on the other, because surface energy appears (surface effect). For small bubbles the decisive role is played by the second term, and for large ones by the first. At a certain definite "critical" bubble dimension the thermodynamic potential of the system reaches a maximum. Therefore, on reaching the critical dimension, the bubble will grow further spontaneously. The amount of work which must be performed against the surface forces to produce a critical bubble is, according to Gibbs, a measure of the metastability of the superheated liquid.

It is easy to show [45] that the work necessary to produce a nucleus is equal to

$$W = \frac{4}{3}\pi R_0^2 \sigma. \tag{1}$$

Of great significance to the development of the theory of boiling were the investigations of Volmer [46]. Volmer's main premise is in essence that the number of nuclei that grow within a certain time interval to visible dimensions is proportional to the number of critical nuclei produced during that time. (Volmer calculated the rate of condensation of the supersaturated vapor, but the results are difficult to generalize to include the case of boiling of a superheated liquid.)

Thus, the rate of boiling is

$$I = Ce^{-\frac{W}{kT}}, \tag{2}$$

where C is a certain proportionality coefficient.

Although Volmer did not succeed in determining the value of C, his theory has made it possible to establish the qualitative dependence of the boiling rate on the physical conditions of the process. Thus, for example, according to (2) the rate of boiling depends very strongly on the surface-tension coefficient. Indeed, as is clear from (1), the exponent W increases rapidly with increasing signal (R_0 depends directly on σ). This explains the well known fact that addition of small amounts of surface-active substances to superheated water contributes to vigorous formation of vapor bubbles. Volmer was also the first to explain the role played in the formation of nuclei by the surfaces of solids with which the superheated liquid is in contact. Poorly wetted sections are places where the activation barrier is low, and consequently are the most probable centers of formation and growth of bubbles.

Let us determine now the dimensions and the pressure in the critical nucleus.

In order for the bubble, once produced, to be able to exist for a noticeable time in the liquid, two equilibrium conditions must be satisfied—mechanical and thermodynamic. Let the pressure of the liquid be P_0 and let the saturated vapor pressure (over a plane surface) be P_∞. The condition for mechanical equilibrium expresses the requirement that the pressure P of the vapor in the bubble be equal to the sum of the external and Laplacian pressures:

$$P = P_0 + \frac{2\sigma}{R}. \tag{I}$$

The thermodynamic condition determines the equality of the fluxes of the molecules evaporated into the bubble, and of the molecules condensed from it into the liquid. This dynamic equilibrium will obviously take place if the vapor pressure P in the bubble is equal to the vapor pressure over the curved surface of the liquid:

$$P = P_\infty \exp\left(-\frac{2\sigma v_l}{RkT}\right), \qquad \text{(II)}$$

where v_l is the volume of the liquid per molecule. Figure 6 shows plots of both conditions on the (R, P) plane, with the bubble characterized by the radius R and the pressure P.

Any bubble represented by a point on curve I is in mechanical equilibrium. In just the same way, any bubble on curve II is in thermodynamic equilibrium. The point of intersection of the two curves corresponds to the equilibrium critical bubble (R^*, P^*).

In order for the bubbles to be able to reach macroscopic dimensions, they must first push through the critical radius. Consequently, as is clear from Fig. 6, the macroscopic bubbles can result only if $P_\infty > P_0$. In other words, the liquid can boil only in those cases when it is either superheated or "undercompressed," i.e., its vapor pressure exceeds the external pressure.

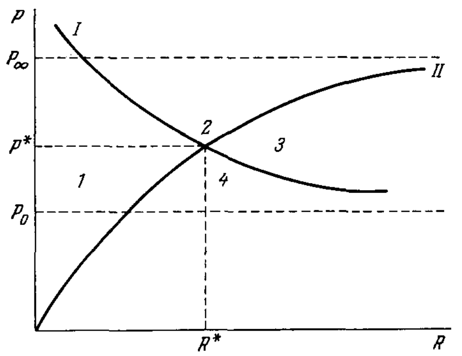

FIG. 6. Dependence of the vapor pressure in the bubble P on the radius R in the case of mechanical (I) and thermodynamic (II) equilibrium. P* and R* – pressure and radius of the critical nucleus.

5. KINETICS OF THE BOILING PROCESS

a) History and nature of the problem. Farcas[47] developed in 1927 Volmer's statistical theory, using a kinetic approach to the vapor condensation process. Farcas' main premise was that in saturated vapor there are two opposite processes: combination into drops as a result of collision between several molecules, and disintegration of the drops into individual molecules. The formation of the drops and their disintegration proceed stepwise via successive trapping or detachment of a single molecule. These processes, generally speaking, have different probabilities, so that the number of existing nuclei depends on the difference between the number of the produced and disintegrating drops per second. For nuclei of subcritical dimension, an equilibrium distribution is established for a number of particles of definite size. For supercritical nuclei, the number of produced drops is larger than the number of the disintegrating ones, so that there is a continuous growth of such drops to visible dimensions. Farcas has shown that the probability of capture of a molecule by a drop is proportional to the saturated vapor pressure, and the probability of disintegration depends on the value of the supersaturation, and therefore depends on the radius of the drop. As a result, Farcas succeeded in obtaining a formula for the flux of the nuclei (condensation intensity); this formula, however, contained an indeterminate multiplier.

In 1934, Kaischew and Stranski[48] generalized the Volmer-Farcas theory to include boiling of liquids. In 1934, Becker and Doring[49], using Farcas' method, considered the stationary process of condensation of supersaturated vapor—the large drops are removed, and the vapor pressure is maintained constant by replenishment of a suitable number of vapor molecules. They succeeded in determining Farcas' indeterminate multiplier. The formula obtained by them could be compared with the experimental data. Experiments by Volmer, Weber[50,51] and Flud[51a] with saturated vapor gave satisfactory agreement with the Becker-Doring formula. It must be pointed out that the Becker-Doring solution was quite cumbersome and did not explain sufficiently the physical nature of the condensation process. *The mechanism of formation of nuclei was apparently not clear to the authors themselves.* This follows, in particular, from the fact that when one of the authors (Doring[42]) attempted to extend the theory to the boiling process, he could not do it fully. It is interesting that in the cited article Doring assumed quite correctly, unlike Kaischew and Stranski[48], that the vapor pressure in the bubble depends on the radius.

Soon afterwards, however, he published a correction[53], in which he rejected his initial views and agreed with the opinion of Kaischew and Stranski that the pressure is the same in all bubbles and is equal to the pressure in the critical nucleus. Moreover, in his latest note Doring presented even a special argument from which it should have followed, as it were, that the pressure in the bubble is independent of its radius. A criticism of this reasoning is given in [54].

J. I. Frenkel[55,56] explained in essence the physical nature of the kinetics of boiling liquids. According to the theory of heterophase fluctuations developed by him, the fluctuation densities that arise even in a thermodynamically-stable system are so appreciable, that they already constitute nuclei of a new phase—heterophase fluctuations. The difference between stable and unstable systems lies in the fact that in the case of the former these nuclei are incapable of surviving—they are produced, reach insignificant dimensions, and again perish. In the unstable (metastable) system, the nuclei of "supercritical" size have a tendency to grow without limit. Frenkel calculated the size distribution function of the nuclei within a stable system.

In order to determine the rates of boiling and condensation in a metastable system, Frenkel considered, like Becker and Doring, these processes under stationary conditions. However, instead of solving an entire system of finite-difference equations, Frenkel used the brilliant method of Ya. B. Zel'dovich[57] to obtain a differential equation for the kinetics of phase transitions. By solving this equation, Frenkel determined the rate of these transformations.

Before presenting a brief derivation of the Zel'dovich-Frenkel fundamental equation, we wish to call attention to the following circumstance.

In all his reasoning concerning boiling, Frenkel considered only spherical bubbles that were always in mechanical equilibrium with the surrounding liquid. By the same token he neglected the shape and pressure fluctuations. Indeed, the deviations of the bubble shape from spherical, corresponding to minimum surface energy, apparently cannot play a major role. However, the legitimacy of neglecting pressure fluctuations calls for additional analysis. After all, this is tantamount to implying that the rate of establishment of mechanical equilibrium greatly exceeds the rate of establishment of the thermodynamic equilibrium, but there are not sufficient grounds for such an assumption. Moreover, as shown in [58], these rates are usually of the same order, and for sufficiently small bubbles thermodynamic equilibrium sets in more rapidly than mechanical.

We must thus consider not only the bubbles that lie on curve I of Fig. 6, but also all other bubbles represented by the points in the (R, P) plane.

The equilibrium of the critical bubble (R^*, P^*) is unstable. Any bubble represented by the point in region 1 will decrease both in volume and in the number of the molecules it contains. To the contrary, any bubble in region 3 will grow continuously, at an ever increasing rate, both in volume in the number of molecules forming it. In regions 2 and 4 the effect of the two "forces"—mechanical and thermodynamic—are in direct opposition and the "fate" of the bubble depends on the ratio of these forces. It turns out that for all possible bubbles there exists a certain watershed line (MN on Fig. 7, where the coordinates represent the number G of molecules in the bubble and the volume V). Curves I and II have the same meaning as in Fig. 6, but in terms of the variables G and V.

Any bubble which "breaks through" this watershed, will have a tendency to grow, while a bubble not reaching this line will tend to become degraded.

Consequently, a rigorous theory of phase transformations should take into account the distribution of the nuclei not only by sizes, but also by the molecule density inside them. Since, however, no such theory has yet been constructed, we confine ourselves to Frenkel's more limited theory.

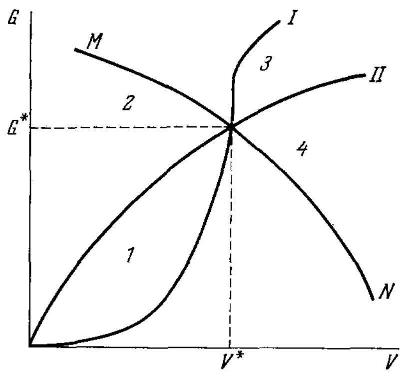

FIG. 7. Connection between the number of molecules in the bubble G and its volume V in the case of mechanical (I) and thermodynamic (II) equilibrium. MN – "watershed" line.

b) The fundamental Zel'dovich-Frenkel kinetic equation of boiling. We proceed to a brief derivation of the differential equation that enables us to determine the speed of boiling, i.e., the amount of liquid transformed per second into vapor, as a function of specified conditions. According to Frenkel, in a thermodynamically stable system there exists an equilibrium distribution of the number N(g) of bubbles containing a given number of vapor molecules:

$$N(g) = N \exp\left[-\frac{\Delta\Phi(g)}{kT}\right], \tag{1'}$$

where N is the total number of molecules in the system, $\Delta\Phi(g)$ the increase in the thermodynamic potential upon formation of a spherical bubble containing g molecules.

In unstable or, more accurately, metastable states, the supercritical bubbles grow continuously at the expense of the subcritical ones when the saturated vapor pressure exceeds the external pressure.

We therefore confine ourselves to an examination of the stationary process, when sufficiently large bubbles are removed from the liquid, and the number of the molecules in the system is maintained constant.

Let α_g be the average number of liquid molecules evaporated per second through 1 cm^2 of surface in a bubble containing g molecules of vapor, and let analogously β_g be the average number of vapor molecules condensing per second on 1 cm^2 of the liquid surface from a bubble containing g molecules. In the stable state, obviously,

$$N_g \alpha_g S_g = N_{g+1} \beta_{g+1} S_{g+1} \tag{2'}$$

(S_g denotes the area of the spherical surface of the bubble, $S_g = 4\pi R_g^2$).

In the unstable state, the flux g → (g + 1) is larger than the inverse flux (g + 1) → g. Denoting by I_g the difference of these fluxes and by f_g the nonequilibrium distribution function of the bubbles, we obtain

$$I_g = f_g \alpha_g S_g - f_{g+1} \beta_{g+1} S_{g+1} \tag{3}$$

or, expressing β_{g+1} in terms of α_g with the aid of (2'),

$$I_g = N_g S_g \alpha_g \left(\frac{f_g}{N_g} - \frac{f_{g+1}}{N_{g+1}} \right). \tag{4}$$

Accordingly, the rate of change of the number of drops of a given class is equal to

$$\frac{\partial f_g}{\partial t} = I_g - I_{g+1}. \tag{5}$$

This equation was derived by Becker and Doring.

Frenkel has gone over to continuous arguments, something perfectly admissible for large g.

Thus, Eq. (4) can be written in the form

$$I_g = -N(g) D(g) \frac{\partial}{\partial g} \left[\frac{f(g)}{N(g)} \right], \tag{4'}$$

where

$$D(g) = \alpha_g S_g.$$

Expanding the square brackets, we can express I_g as follows:

$$I_g = -D \frac{\partial f}{\partial g} + Df \frac{\partial \ln N}{\partial g}. \tag{4''}$$

But according to (1)

$$\frac{\partial \ln N}{\partial g} = -\frac{1}{kT} \frac{\partial \Delta\Phi}{\partial g},$$

Therefore

$$I_g = -D \frac{\partial f}{\partial g} - \frac{1}{kT} \frac{\partial}{\partial g} \left(fD \frac{\partial \Delta\Phi}{\partial g} \right). \tag{6}$$

Since, according to (5)

$$\frac{\partial f(g)}{\partial t} = -\frac{\partial I(g)}{\partial g},$$

we arrive at the fundamental equation for the kinetics of boiling, obtained by Ya. B. Zel'dovich and J. I. Frenkel,

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial g} \left(D \frac{\partial f}{\partial g} \right) + \frac{1}{kT} \frac{\partial}{\partial g} \left(Df \frac{\partial \Delta\Phi}{\partial g} \right). \tag{7}$$

Recognizing that D(g) depends little on g in comparison with f(g), we can represent (7) approximately in the form

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial g^2} + \frac{D}{kT} \frac{\partial}{\partial g} \left(f \frac{\partial \Delta\Phi}{\partial g} \right), \tag{7'}$$

which can be regarded as the usual diffusion equation, where D is the "diffusion coefficient," D/kT = q is the mobility, and

$$-\frac{\partial \Delta\Phi}{\partial g} = F$$

is the "external force." Zel'dovich found a simple method of solving this equation in the stationary case, i.e., when $\partial f/\partial t = 0$, which is equivalent to the condition I(g) = I = const. Indeed, according to (4'),

$$f(g) = IN(g) \int_g^G \frac{dg}{N(g) D(g)}, \tag{8}$$

where the upper limit is chosen such as to satisfy the boundary condition

$$f|_{g=G} = 0.$$

Expressing N(g) with the aid of (1) we obtain

$$f(g) = Ie^{-\frac{\Delta\Phi(g)}{kT}} \int^G \frac{1}{D(g)} e^{\frac{\Delta\Phi(g)}{kT}} dg. \tag{8'}$$

The function exp (ΔΦ(g)/kT) has a very sharp maximum for the critical bubble g′, for in this case ΔΦ assumes the largest value.

Therefore D(g) can be replaced by the quantity D(g*), and ΔΦ can be replaced by the first two terms of the Taylor-series expansion

$$\Delta\Phi(g) = \Delta\Phi^* - \frac{1}{2}\gamma (g - g^*)^2,$$
$$\gamma = -\left(\frac{\partial^2 \Delta\Phi}{\partial g^2} \right)^*. \tag{9}$$

Introducing a new variable ξ = g − g*, we arrive at the equality

$$f(g) = \frac{1}{D(g^*)} e^{\frac{\Delta\Phi^* - \Delta\Phi}{kT}} \int_{-(g^*-g)}^{G-g^*} e^{-\frac{\gamma\xi^2}{2kT}} d\xi. \tag{10}$$

Assuming that G − g* and g* − g are sufficiently large, we can expand the integration limits from −∞ to +∞ and obtain for the resultant flux I_{res} the formula

$$I_{res} = N(g^*) D(g^*) \sqrt{\frac{\gamma}{2\pi kT}}. \tag{11}$$

To clarify the physical meaning of this formula, we take into consideration the fact that

$$\Delta\Phi(g^*) = \frac{4}{3}\pi\sigma R^{*2},$$

$$\Delta\Phi(g) = (\varphi_v - \varphi_l) g + \text{const} \cdot \sigma g^{2/3},$$

where φ_v and φ_l are the specific thermodynamic potentials per vapor and liquid molecule. Then it is easy to see that the rate of boiling $Q = I_{res} g^*$ is equal to

$$Q = N \cdot 2R^{*2} \frac{P^*}{kT} \sqrt{\frac{\varphi_m - \varphi_n}{3m}}\, g^* \exp\left(-\frac{4\pi\sigma R^*}{3kT} \right). \tag{12}$$

As an illustration of (12), we consider the following example. Let water (σ ≅ 72 dyne/cm) be at room temperature (T = 300°), and let us determine the required rarefaction (P_{ext}/P_{vap}) in order for the relative rate of boiling Q/N to become noticeable in practice.

Since the decisive factor in (12) is

$$\exp\left(-\frac{4\pi\sigma R^{*2}}{3kT} \right) \cong e^{-7 \cdot 10^{15} R^{*2}},$$

for any noticeable rate of boiling Q/N the radius R* of the critical nucleus must be of the order of 10^{-7} cm. This size of the critical bubble is obtained at rarefactions P_{ext}/P_{vap} close to 0.00003.

It is therefore clear that at ordinary rarefaction or superheat heterophase fluctuations will not cause a liquid to boil.

It is shown in [59] that real liquids can boil at a noticeable rate in this way only when the superheat is

$$T - T_{boil} > \frac{T_{cr} - T_{boil}}{2}.$$

Since a liquid actually begins to boil at insignificant superheat, we can conclude that in any liquid there are always present factors that facilitate the onset of boiling.

A giant step forward in the kinetics of boiling was made recently by Yu. Kagan[60]. Kagan assumes first that the main assumption of the existing boiling theories (Volmer's, Doring's, Frenkel's) concerning mechanical equilibrium of any bubble, is incorrect. This is particularly clearly seen in the case of negative external pressures. Therefore Kagan proceeds as follows. Following Zel'dovich, he assumes the initial equation (4) and then goes through exactly the transformations given in Eqs. (3)—(9), but uses in lieu of $\Delta\Phi$ the more correct quantity W. Expanding then W in powers of $P - P_0$, he obtains in lieu of the usual $W = 4\pi R^2\sigma/3$ the expression

$$W = 4\pi R^2\sigma - \frac{8}{3}\frac{\pi R^3\sigma}{R^*}. \tag{13}$$

This greatly complicates the calculation of the 'diffusion'' coefficient D(g):

$$D^*(g^*) = -kT_0\left(\frac{d\dot{g}}{dR}\right)^*\left(\frac{dg}{dR}\right)^* \Big/ \left(\frac{\partial^2\Phi}{\partial R^2}\right)^*. \tag{14}$$

In order to find $(d\dot{g}/dR)^*$, it is necessary to consider the general dynamics of the bubble:

$$\dot{g} = \text{const}\cdot R^2(P_R - P). \tag{15}$$

The pressure P is assumed to be unknown and is determined from the fundamental equation for the bubble growth (see formula (II′) in Sec. 7):

$$\varrho R\ddot{R} + \frac{3}{2}\varrho\dot{R}^2 = P - \frac{2\sigma}{R} - P_0 - \text{const}\cdot\eta\,\frac{\dot{R}}{R}.$$

In order to take more accurate account of the true value of the pressure P, allowance is made for the absorption of heat during the expansion of the bubble (and the release of heat upon compression). A simple analysis shows that the Laplace equation $\Delta T = 0$ is adequate, giving for the temperature of the bubble walls $T = T_0 - \text{const}\cdot\dot{g}$. Introducing a suitable temperature correction, Kagan arrives at a rather cumbersome equation for $(d\dot{g}/dR)^*$. By solving this equation, he expresses D and I in dimensionless form. The principal advantage of Kagan's solution over, say, formula (12) is its generality, its validity for arbitrary values of the viscosity, inertia, rate of evaporation, and condensation, and rate of heat supply. To be sure, for practical purposes Kagan's expression is cumbersome. This expression simplifies appreciably in the particular case when the inertial term can be neglected. If, furthermore, the inequality $2\sigma/R^*P^* \ll 3$ holds true, then the decisive role for the boiling speed is played by the evaporation rate; this yields the usual Doring formula (12). The value of the paper [60] can be seen from the fact that it makes it also possible to determine the probability of formation of nuclei in those cases when the rate of evaporation is negligibly small and the decisive role is played by the viscosity (for example, cavitation of liquids at negative pressures).

The kinetics of the boiling process is dealt with also in [160-162,180]. Of great interest is an experimental verification of the theoretical deductions presented in this section. This was done by V. P. Skripov and G. V. Ermakov[165], using for this purpose a method developed in [163,164]. They observed the upward floating of individual drops of different liquids in a column of concentrated sulfuric acid with an upward-directed temperature gradient. Owing to the increase in the superheat, the drops disintegrated at a certain altitude. Since the surface tension on the boundary with the acid was larger than on the boundary with the vapor, bubbles were produced inside the drop, i.e., boiling of the pure liquid took place. These experiments, carried out at different pressures, have made it possible to determine the limiting superheat of pure liquids. The results of the experiments are in good agreement with the data that followed from formula (12). With increasing external pressure, the maximum superheat rapidly decreases. Skripov and Ermakov were able to conclude from these experiments that the decisive role in Kagan's theory, during the first stage of formation of the nucleus, is played by the rate of evaporation of the molecules in the cavity, while the viscosity, thermal conductivity and the inertial forces are of secondary significance.

6. ONSET OF BOILING IN LIQUIDS UNDER REAL CONDITIONS

As already noted in the preceding section, under real conditions there are always factors which greatly facilitate the onset of boiling in liquids, so that practically at negligible superheats the boiling rate becomes noticeable. It is therefore of importance for the theory of boiling to investigate the character and the role of different types of such factors. In recent years several investigations have been devoted to this question.

We recall that in order to attain macroscopic dimensions any bubble must ''break through'' the critical nucleus; the increase in the thermodynamic potential is in this case equal to[61]

$$\Delta\Phi^* = \frac{16\pi v_g^2\sigma^3}{3(\varphi_l - \varphi_v)} \tag{1''}$$

(φ_l and φ_v are the thermodynamic potentials of the liquid and vapor per molecule, v_g is the volume per molecule in the gaseous phase).

Accordingly, the radius of the critical nucleus is determined by the relation

$$R^* = \frac{2\sigma v_g}{\varphi_l - \varphi_v}. \tag{2''}$$

Thus, foremost among the agents that facilitate the boiling of liquids are the factors (we shall assign them in group 1) which decrease the height of the potential barrier $\Delta\Phi^*$.

Inasmuch as for spherical bubbles at a specified superheat, $\Delta\Phi^*$ depends according to (1″) (and quite strongly) only on σ, the effect of these factors reduces to a decrease of the surface tension σ at least in individual spots.

These factors include: the presence in the liquid of surface-active impurities, and the presence of poorly wetted solid surfaces in contact with the liquid.

It must be noted immediately that the surface-active impurities are in themselves of no practical interest for the onset of boiling. Thus, even the most active adsorbent, such as organic substances with strongly asymmetrical molecules, will not reduce σ of water enough to permit it to start boiling at a noticeable rate in the case of ordinary superheats.

As regards the role of smooth solid surfaces, it was already shown by Volmer[46] that when a critical nucleus is formed, $\Delta\Phi'$ on the boundary of this nucleus is a simple function of the contact angle θ:

$$\Delta\Phi' = \Delta\Phi\, f(\theta), \qquad (3'')$$

where

$$f(\theta) = \frac{1}{4}(1+\cos\theta)^2(2-\cos\theta) .$$

A plot of $f(\theta)$ is shown in Fig. 8.

It is easy to see that when $\theta > 160°$ $f(\theta)$ becomes sufficiently close to zero, and the probability of formation of the critical nucleus becomes noticeable.

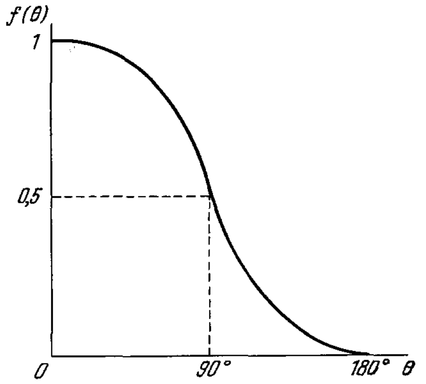

FIG. 8. Plot of the function $f(\theta) = \Delta\Phi'/\Delta\Phi$ on the values of the contact angle θ.

Strictly speaking, however, we must take account also of the influence of the so-called linear energy[56]. The linear energy δ is the excess of energy of the molecules lying on a contour of a planoconvex bubble, compared with the molecules of the surface. From general considerations it is clear that δ is incomparably smaller than σ, but when $\theta \rightarrow 180°$ the role of the linear tension δ becomes manifest[54]; thus, even when $\theta = 180°$ there exists already a certain potential barrier $\Delta\Phi$ (albeit very small).

All this is of theoretical interest, since contact angles close to 180° are not encountered in nature. Therefore, even the presence of smooth poorly wetted solid surfaces cannot make the probability of nucleus formation appreciable. It does not follow, nevertheless, that the practical influence of such surfaces on the facilitation of the boiling process is insignificant. The point is that the detachment and the removal of sufficiently large bubbles grown on "surface" nuclei proceeds in an entirely different manner than in the case of bubbles produced within the volume of the liquid.

This question was first considered theoretically in papers by the author[54,62].

It turns out that an important role is played here by the forces of gravity, and consequently the angle of inclination of the solid surface to the horizontal is significant.

Let us present the main results of these investigations. If a bubble has been produced on a vertical surface (on walls of vessels), then, as it increases, it will assume an ever more asymmetrical form: the upper contact angle θ_2 increases, and the lower θ_1 decreases (Fig. 9)[63]. At a certain difference $\theta_2 - \theta_1$, whose value is fixed for the particular bodies in contact, complete sliding of the bubble begins, i.e., the "pouring over" of the vapor upward, without leaving any parts of the bubble on the wall. This deduction was confirmed by experimental data[64,65].

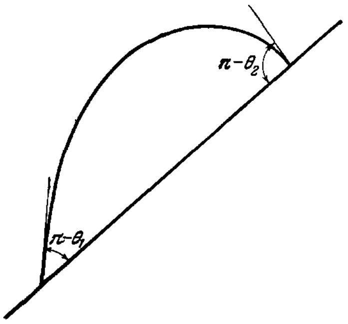

FIG. 9. Shape of the vapor bubble on an inclined surface.

The removal of macroscopic bubbles from a horizontal solid surface (bottom of a vessel) is entirely different. The shape of the growing bubble varies continuously, stretching first upward and then forming a narrow section in the form of a neck in the lower part (Fig. 10).

It turns out that for sufficiently large bubbles such a shape is energetically preferred—this corresponds to a minimum sum of the free surface energy and the potential energy of the gravity forces. With further increase of the bubble, the neck becomes narrower, until the upper part separates completely from the lower one, and starts to float upward. It is important however, that a nucleus from which many new bubbles can grow still remains at the bottom. This deduction was confirmed experimentally[228]. Thus, even if the probability of formation of a primary nucleus on a poorly wetted horizontal surface is low, the rate of boiling can become quite appreciable. This idea was further developed in [229]. The dependence of the intensity of boiling on the surface properties of the liquid is the subject of the review[171].

The second group of factors facilitating the onset of boiling are those contributing to the formation of bub-

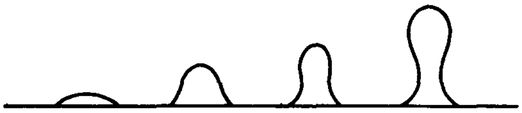

FIG. 10. Variation in the shape of the vapor bubbles on a horizontal surface with increasing bubble volume.

bles that are immediately of supercritical size, without going through a "subcritical stage." These include: already existing large bubbles of air contained in the absorbed state in the liquid itself or in the vessel walls, or the presence of narrow pits, pores, in solids in contact with the liquid.

It is obvious that a smooth horizontal bottom on which primary nuclei have been produced can also be included in this group. The role of the ready air bubbles for the boiling of liquids was explained already by Poynting (see, for example [66]). It must be borne in mind that if the bottom (and also the walls) of the vessel are well wetted by the liquid, the intensity of boiling will decrease with time, until it becomes equal to zero when all the air bubbles have been removed from the liquid[166,235-238].

Much more important are the minute pits, cracks, and pores which are usually present in the walls of the vessel.

The first to consider the influence of pores of cylindrical form on boiling was Andreev[65]. Andreev's results were refined in [54,62]. In the case of small contact angles, the cylindrical pores can be active centers of boiling, if the radius of the pores is larger than a certain critical value r^*, and the liquid does not fill the volume of the pore completely prior to the start of the boiling (this is possible if it was in contact with the walls of the given vessel for a short time before that). In the case of non-wetting (contact angle $> 90°$), the active pores will be those whose dimensions are contained within a certain optimal range. Quantitative calculations for conical pores were made by Turnbull[67]. Labuntsov[218] determined the form of the function $\Delta\Phi(\varphi)/\Delta\Phi_0$ of the apex angle 2φ for different contact angles θ. Qualitative experiments on the study of the boiling on a solid surface are reported in [166-168,237-239].

In addition to the two groups under consideration, it has been found recently that there exists a third group of factors facilitating the onset of boiling due to the effect of external forces. This group includes sonic and ultrasonic fields. It is known from experiments made by many workers[39,68,188,189] that irradiation of slightly superheated liquid by intense ultrasonic waves causes vigorous bubble formation, i.e., boiling. Direct experiments by V. V. Chekanov have shown that low-frequency waves are the most effective in this case. A theoretical analysis of the influence of ultrasonic field on the process of bubble formation in superheated liquid is found in [69,70]. Under the influence of sound, the bubble grows during the rarefaction half-cycle and contracts during the compression half-cycle, but these alternating "expansions" are somewhat larger than the "contractions." Owing to such nonlinear pulsations, the dimension of the critical nucleating bubble decreases, and the rate of boiling increases.

For ultrasonic boiling the decisive role is apparently played by the presence of microscopic gas bubbles in the liquid[244]. The action of a sound wave on a vapor-gas bubble in a superheated liquid reduces to its "buildup" and "jumping through" the potential barrier separating the critical and subcritical nuclei[247]. In addition, sound facilitates boiling by raising the temperature of the liquid around the bubbles that pulsate under its influence[70].

Since boiling is accompanied by an acoustic noise, the sound emitted by the already produced bubbles should exert an influence on the bubble-formation process. Experiments especially set up by V. V. Chekanov[71,72] have fully confirmed this. A wire immersed in water was heated with current to temperatures somewhat higher than 100° C. The water was thoroughly cleaned and outgassed beforehand, and therefore did not boil. But when liquid around a wire was made to boil in a second vessel (separated from the first by a heat-insulating sound-conducting partition), boiling started also on the first wire. It can therefore be assumed that when a liquid boils up, a chain reaction of bubble formation occurs under certain conditions. The influence of sound waves on the growth of bubbles in a liquid is treated also in [201-203].

Another in this group of factors facilitating the boiling is ionizing radiation. With an aim at constructing a bubble chamber, Glaser[73,74] investigated the effect of ions on the formation of the nuclei. He passed high-energy radiation through various superheated liquids—ether, pentane, and liquid hydrogen. The tracks of the bubbles could be clearly seen in the liquids. The number of such bubbles per centimeter of path reached approximately 100. The investigations showed that in order to increase noticeably the rate of boiling by irradiation, the liquid should be slightly ionized and should be a poor conductor of electricity. Water does not satisfy these conditions well; to the contrary, liquid hydrogen and low-molecular paraffins are quite sensitive to radiation. Recent experiments [190,191] have shown directly that fast neutrons and charged particles contribute to the formation of nuclei in the liquid.

The initial theory of the effect of radiation was developed by Glaser[75]. Rapid particles entering into a liquid produce along their path a swarm of charged ions of the same polarity. These ions are repelled from one another and cause a nucleation-type microexplosion of the liquid. In other words, according to Glaser the radiation causes the appearance in a liquid of electric forces that counteract the surface forces. These notions are in good agreement with the experimental facts indicating that radiation has little influence on the formation of bubbles in liquid conductors. G. A. Askar'yan[76] developed Glaser's theory further, showing theoretically that an important role in the explosion of the liquid is played by the electric fields of the ions; this role is manifest not only in the repulsion of the ions but also in effecting a coupling between the ions and the molecules of the liquid. The authors of [172] also adhere to this electrostatic theory of bubble formation in a chamber.

Recently, however, the thermal theory, first developed in a brief communication[173] and then in greater detail in [174] has been gaining favor. According to this theory, when a charged particles passes through matter, δ-electrons are produced. These lose their energy on relatively short sections of the path. This energy is released in the form of heat that goes into evaporation of the molecules into a bubble. Therefore the number of produced bubbles sharply depends on the superheat of the liquid. This question was considered in greater detail in the review[174]. The question of the influence of the electric field on the character of boiling of a liquid and growth of bubbles is the subject of [196-198].

7. BUBBLE GROWTH

Boiling consists of two main processes—occurrence and growth of the bubbles. So far we have dealt primarily with the former. We now consider in greater detail the second aspect of the boiling process—bubble growth.

In 1917 Rayleigh[77] considered theoretically the following problem. A cavitational spherical cavity is suddenly produced in an incompressible and nonviscous liquid; it is required to determine the time during which the liquid fills this cavity, and the value of the pressure produced thereby. To solve this problem, Rayleigh derived a differential equation in which the rate of change of the cavity radius dR/dt can be expressed as a function of the pressure and density of the liquid. A solution of this equation has shown that very large radial velocities and tremendous pressures should be possessed by the liquid filling the cavity. Experiments[78] with high speed motion picture photography have confirmed Rayleigh's deductions. In 1942 Beaching[79] applied Rayleigh's equation to the case when a vapor bubble of variable volume is present in the liquid in place of a cavity. Let us consider the derivation of Rayleigh's equation.

Assume that a spherical bubble of radius R grows in a nonviscous incompressible liquid and produces around itself a velocity field v(r, t). Euler's equation in spherical coordinates takes the form

$$\varrho\left(\frac{\partial v}{\partial t}+v\frac{\partial v}{\partial r}\right)=-\frac{\partial P}{\partial r}, \qquad (1''')$$

and the continuity equation is (see, for example, [80])

$$\frac{\partial v}{\partial r}+\frac{2v}{r}=0. \qquad (2''')$$

Integrating (2) we get

$$v(r,t)=\frac{f(t)}{r^2}, \qquad (3''')$$

where the arbitrary function f(t) can be expressed in terms of the rate of bubble growth $\dot R(t)$, namely, when r = R

$$v=\dot R(t), \text{ and } \dot R=\frac{f(t)}{R^2},$$

hence

$$f(t)=\dot R R^2. \qquad (3'a)$$

Consequently

$$v(r,t)=\frac{1}{r^2}\dot R R^2. \qquad (4''')$$

Substituting

$$\frac{\partial v}{\partial t}=\frac{f'(t)}{r^2}$$

in (1), we arrive at the equation

$$\frac{f'}{r^2}+\frac{1}{2}\frac{\partial v^2}{\partial r}=-\frac{1}{\varrho}\frac{\partial R}{\partial r}.$$

Integration from r = R to r = ∞ yields

$$-\frac{f'}{R}+\frac{\dot R^2}{2}=\frac{P_R-P_\infty}{\varrho}. \qquad (5''')$$

We substitute here $f'(t) = R^2\ddot R + 2R\dot R^2$ and replace the external pressure on the bubble P_R in terms of the vapor pressure P inside the bubble:

$$P_R=P+\frac{2\sigma}{R}.$$

We get as a result the following final equation for the bubble growth:

$$R\ddot R+\frac{3}{2}\dot R^2=\frac{P-P_\infty}{\varrho}-\frac{2\sigma}{\varrho R}. \qquad (I')$$

Here ρ is the density of the liquid and P_∞ the pressure in the liquid far from the bubble. If the liquid has a viscosity η = const, the equation takes the more complicated form[81]:

$$R\ddot R+\frac{3}{2}\dot R^2+\frac{4\eta\dot R}{\varrho R}+\frac{2\sigma}{\varrho R}=\frac{P-P_\infty}{\varrho}. \qquad (II')$$

The two equations (I) and (II) establish the connection between the bubble radius R and the vapor pressure in it. The extreme complexity of these equations consists in the fact that even if we assume the vapor to be an ideal gas the pressure P depends on the vapor) density ρ' and the temperature T, which in turn are functions of $\dot R(t)$.

The first to solve this equation were Zwick and Plesset[82,83]; they took into account the fact that the temperature around a growing bubble drops because of the evaporation of molecules in it. This in turn leads to a decrease in the vapor pressure in the bubble, meaning also to a decrease in its growth rate.

In the case of Eq. (I), the solution can be represented in the form of four stages of bubble growth.

In the first, relaxation stage, the bubble increases from the nucleation radius R_0 to $(1 + 1/e)R_0$. During that time R varies like

$$R = R_0\,(1 + e^{H(t-t_0)}),$$

where t is reckoned from the instant when the nucleus has become unstable; H is a certain temperature-dependent quantity. The succeeding stages were called by Zwick and Plesset the early, intermediate, and asymptotic phases.

During the asymptotic phase the temperature in the bubble approaches the boiling point of the liquid, and the radius increases in proportion to the square root of the time. Several authors[36,195] took high speed motion pictures of the bubble growth and obtained splendid agreement with the calculations of Zwick and Plesset. The initial theory of Zwick and Plesset was generalized and expanded in several new papers[192-184]. When the bubbles become sufficiently large ($R > 1$ mm) and the expelling forces come into play, the character of the bubble motion, naturally, changes. The question of the motion of the upward floating bubbles has been treated in numerous experimental and theoretical papers[84,86-90,23 et al.], which were reviewed in detail in the well known book by V. G. Levich[85]. Haberman and Morton[84] investigated experimentally the behavior of such bubbles. It turned out that so long as $R < 1$ mm the bubbles are spherical and float in accordance with Stokes' law, whereas when $1\text{ mm} < R < 5$ mm the bubbles become ellipsoidal, acquiring a mushroomlike shape when $R > 5$ mm.

Small bubbles float upwards in a straight line, without experiencing any disturbance. Medium bubbles (for which the Reynolds number is 300—3,000) move on helical lines, and the largest ones experience during the ascent continuous jumps in a horizontal plane. Large bubbles with $R > 1$ cm have little stability and break up along their path into smaller ones. Before breaking, the bubble flattens, starts pulsating, a thin film is produced in its center and bursts at a definite instant, and the initial bubble breaks up into a group of smaller bubbles. The theory of crumbling of bubbles was developed by V. G. Levich[85].

It must be borne in mind that Rayleigh's equation is purely hydrodynamic and essentially does not take into consideration the molecular processes of evaporation and condensation. In the derivation of this equation it is tacitly assumed that the time of establishment of mechanical equilibrium is negligibly short. Therefore allowance on the part of Plesset and Zwick for the change in the temperature of the bubble wall due to the phase transitions occurring on its boundary was an important step forward. However, a rigorous theory must consider the growth of the bubble in a superheated liquid as a single mechanical-molecular process, where account is taken of the finite values of the velocities $\dot{V}$ and $\dot{G}$, thermal effect, and the influence of the force on gravity.

For the physics of boiling it is very important to know the dimensions of the vapor bubbles that break away from the heating surface. This question was first considered by Fritz (see [240]) who determined, by analyzing the well known tables of Bashforth and Adams[148], the maximum possible volume $V_{\max}$ of a bubble on a horizontal surface. Assuming that the volume of the bubble during the instant of detachment is $V_{\max}$, Fritz obtained for the diameter of the detaching bubble.

$$D_0 = \varphi(\theta) \sqrt{\frac{\sigma}{g(\varrho - \varrho')}},$$

where σ is the surface tension, ρ and ρ' the densities of the liquid and the vapor, and $\varphi(\theta)$ a certain universal function of the contact angle, approximately equal to $0.02\,\theta°$.

Fritz's formula is in satisfactory agreement with the experimental measurements[241,242,91,92,98]. It must be noted, however, that in all these experiments the contact angles did not exceed 100°.

Actually Fritz's formula determines the maximum diameter, and not the diameter at detachment. At not too small θ, the bubble detaches from the solid surface not as a whole, but along a "neck" [62], the height of which is the larger, the larger the angle θ. Therefore the true value of the detachment diameter differs from D_0 by a certain factor $k(\theta)$ which is smaller than unity.

Using the first law of thermodynamics, we can find [249] that the product of the diameter D_0 of the detached bubbles by the frequency of the detachment u is a constant quantity for a given liquid and for a specified temperature gradient and pressure. With increasing pressure, the product D_0u increases in inverse proportion to P [5,98].

Observations of the dimension and frequency of the bubble detachment[93,94], and also of the growth of the already detached bubbles, make it possible to determine the coefficient of heat transfer from the liquid to the bubble. The values of the coefficients for different liquids fluctuate between 1 and 5 cal/cm^2 sec-deg.

8. SOUND ACCOMPANYING BOILING

It was already noted that the simplest experiments on the measurement of the boiling noise have disclosed an undisputed dependence of the sound intensity on the character of the sound-producing boiling. A more detailed investigation of the noise produced when a liquid is made to boil on a hot wire was made by Osborne and Holland[31,38]. They investigated the dependence of the sound intensity on the electric power supply and on the duration of boiling, and also the frequency characteristic of the noise. Their principal results reduce to the following. With increasing power flow through the wire, the intensity of the sound first increases, then becomes constant—saturation sets in. Sometimes, the sound intensity decreases somewhat after reaching a maximum. The intensity of the saturation sound depends little on the thickness, type, and orientation of the wire, being a characteristic of the hot wire as a source of sound. The intensity I for a given power W depends also on whether its value was obtained as a result of increasing or decreasing the power. After numerous repetitions of successive increases and decreases in the values of W, the I(W) curve gradually shifts higher and higher, until a certain limiting level is attained.

Of great interest are the spectral characteristic of the boiling noise, obtained by Osborne and Holland. In the lower-frequency interval from 300 to 1,000 cps, the sound power is approximately constant, independently of the current and the geometry of the wire. Between 1 and 30 kcs there is a broad maximum. The frequency corresponding to this maximum increases with decreasing wire diameter. For frequencies above 30 kcs, the sound intensity I decreases rapidly (Fig. 11).

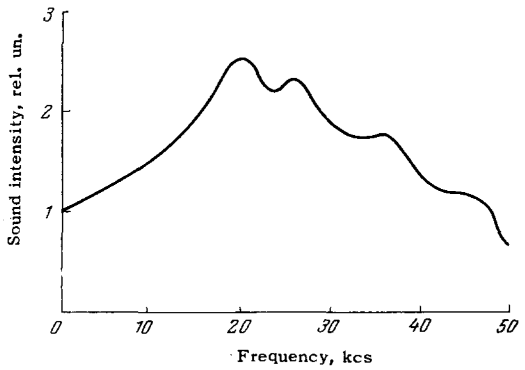

FIG. 11. Frequency spectrum of the acoustic noise of a boiling liquid.

The character of the sound depends on the material of the wire. Thus, the intensity is lower for tungsten than for nichrome. The frequency characteristic of the latter depends on the power of the supplied current, while for the former it is not. The form of the continuous noise spectrum depends also on whether the wires are heated with direct or alternating current. With increasing water temperature around the wire, the pitch of the sound dropped, and the dimensions of the bubbles increased somewhat. The authors note that two stable characteristic types of radiated sound appear as the filament current is gradually increased: one "cold sound" at a lower temperature and "hot sound" at a higher temperature. The former corresponds to bubble boiling, the latter to film boiling. A distinction exists between noise of boiled and tap water: in the former the intensity is much higher and the maximum frequency is much more sharply pronounced.

Osborne, following Rayleigh, assumes that the boiling noise is radiated by the collapsing bubbles. Therefore the hot wire is a relatively powerful source of noise in the case of local boiling of the liquid. Starting from this premise, Osborne explains in the following manner the rise in the maximum sound frequency with decreasing wire thickness. Assume that a bubble of radius $R \ll r$ is produced on a wire of radius r. The heat enters the bubble through the concave surface of contact with the solid, and goes into the liquid through the convex part of the sphere. This bubble grows. So long as $R < r$, the ratio S_R/S_r of the areas of the convex "cooling" and concave "heating" parts of the sphere remains approximately constant. With further increase in the bubble, this ratio starts to decrease rapidly. Therefore the growing bubble maintains thermal equilibrium only until the radius R becomes equal to r. Starting with this instant, the influx of heat into the bubble decreases and the bubble rapidly collapses. Consequently, the thinner the wire, the smaller the dimension of the collapsing bubbles, meaning the higher the frequency of the sound radiated by them. The dependence of the sound intensity on the degree of outgassing of the liquid, according to Osborne, is explained by the fact that the presence of gas in the collapsing bubble softens the impact of the liquid filling the cavity. It must be noted that although Osborne's ideas concerning the sound of local boiling on a wire explains many experimental facts satisfactorily, they can hardly serve as a basis for a general theory of the sound produced by boiling. This is seen from the fact that Osborne is unable to explain the causes of numerous other experimental laws, such as the increase in the frequency of the maximum with increasing current through the wire or the absence of a proportionality between the intensity of the sound and the length of the wire.

Apparently, Osborne's basic assumption, that the sound is radiated only upon collapse of the bubbles, is incorrect. Direct experiments with gas bubbles[96,97] and those performed by V. V. Chekanov and E. D. Popov[230] with vapor bubbles show that an intense pressure wave is produced in the liquid at the instant of bubble formation. A later and much subtler experiment by V. V. Chekanov has shown directly that the sound is produced principally when the bubble is formed, and not when it collapses,

The cause of the noise produced during boiling was at first not considered seriously by anyone. W. Bragg[99] proposed for the first time that the murmuring of streams is produced by air bubbles contained in the water. An experimental and theoretical analysis of this premise was made by Minnaert[96]. He showed that the bubbles do not act like rigid resonators in this case, but are subject to volume pulsations. Assuming the alternating compression and expansion to be adiabatic, he obtained for the frequency of the natural oscillations of the bubble the following formula:

$$\nu_0 = \frac{1}{2\pi R}\sqrt{\frac{3\gamma P}{\varrho}},$$

where R is the radius of the bubble, P the static pressure, ρ the liquid density, and γ the ratio c_P/c_V. Experiments set up by Minnaert gave good agreement with this formula. Similar results were obtained also by others [100,101,199,200].

In [97,102] there was considered the possible occurrence of not only volume but also shape fluctuations of the bubbles. It turned out that allowance for the changes in the shape of the vibrating bubble has little effect on the distribution of the pressure in the liquid (with the exception of the region directly adjacent to the bubble).

Recently, Strasberg and Devin [103] advanced the hypothesis that the main source of sound in a liquid is pulsation of gas bubbles. These pulsations are formation of the bubbles, their growth or division, the motion of a current of liquid containing gas bubbles, or the action of an external sound wave. Following Strasberg and Devin, the present author advanced the hypothesis [214] that sound in a boiling liquid is due to pulsating vapor-gas bubbles. Radial pulsations are usually also produced when the volume of the bubble changes rapidly. The faster the rate of growth (or decrease) of the bubble, the larger the amplitude of the oscillations and the more intense the radiated sound.

The hypothesis that sound is produced during boiling by pulsations of vapor-gas bubbles was confirmed by a subtle experiment by B. M. Dorofeev.

Apparently the presence of gases in the liquid does not attenuate the sound accompanying the collapse of the bubbles, as assumed by Osborne, but increases the probability of gas bubble formation, i.e., the number of sound emitters. On the other hand, the sound intensity is lower in a gasified liquid because it increases more rapidly than that of gas-free liquid.

A rigorous theory of the pulsations of gas bubbles was proposed by Devin [103]. To derive the equation of motion of the oscillating bubble, he expressed the Lagrangian in terms of a single independent variable—the volume of the bubble. The differential energy of the system is obviously

$$W_n = -\int_0^v (P - P_0)\, dv,$$

where P_0 is the pressure in the liquid, P the instantaneous pressure in the bubble, and $v = V - V_0$ the deviation of the bubble volume V from its equilibrium value V_0. The Laplace pressure connected with the curvature of the phase-separation boundary is neglected. Assuming that the state of the gas in the bubble changes adiabatically, we can easily obtain

$$W_n = \frac{\gamma P_0}{2V_0} v^2.$$

It is also easy to calculate the kinetic energy of the liquid surrounding the bubble. Indeed, the velocity potential φ of an incompressible liquid satisfies the Laplace equation $\nabla^2\varphi = 0$.

Inasmuch as the liquid is at rest at infinity, the corresponding solution for a point located at a distance r from the center of the bubble should be

$$\varphi = \frac{f(R)}{r}.$$

The velocity of the liquid is

$$\dot r = -\operatorname{grad}\varphi = \frac{f(R)}{r^2}.$$

On the surface of the bubble r = R and $\dot R = f(R)/R^2$, hence

$$f(R) = \dot R R^2 = \frac{\dot v}{4\pi}.$$

Thus,

$$\dot r = \frac{\dot v}{4\pi r^2}.$$

Therefore the kinetic energy of a liquid of density ρ is

$$W_k = \frac{\varrho}{2}\int_{R_0}^{\infty} \dot r^2 4\pi r^2\, dr = \frac{\varrho}{8\pi R_0}\dot v^2$$

and the Lagrangian is

$$L = \frac{\varrho}{8\pi R_0}\dot v^2 - \frac{\gamma P_0}{2V_0} v^2.$$

Consequently, in the absence of dissipation, the Lagrange equation takes the form

$$\frac{\varrho}{4\pi R_0}\ddot v + \frac{\gamma P_0}{V_0} v = 0.$$

If we write $\rho/4\pi R_0$ in terms of the generalized mass m and take into account the fact that

$$\frac{\gamma P_0}{V_0} = -\left(\frac{\partial P}{\partial V}\right)_S$$

is the adiabatic stiffness k_{ad}, we obtain the usual equation for linear harmonic oscillations

$$m\ddot v + k_{ad} v = 0,$$

from which we get for the natural frequency of the bubble vibrations

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_{ad}}{m}} = \frac{1}{2\pi R_0}\sqrt{\frac{3\gamma P_0}{\varrho}},$$

which agrees with Minnaert's formula [96].

On the other hand, since the thermal conductivity, viscosity, and radiation of the sound cause energy dissipation, the bubble vibrations are actually damped. Devin calculated the damping decrement by using the experimental data of [104–107] and improving the theoretical methods of his predecessors [108–112]. The values obtained by him are in satisfactory agreement with the experimental measurements.

It must be emphasized, however, that Devin's results have a limited bearing on the boiling process, since they were obtained without account of the vapor pressure. We have therefore investigated in [113] the character of the pulsations of bubbles of vapor and of a mixture of vapor and gas in a liquid.

It is assumed that in the initial state the bubble is in mechanical and thermodynamic equilibrium with the liquid, and starts to pulsate as a result of some action. Generally speaking, this produces a change not only in the volume V, but also in the number G of the molecules in the bubble. The character of the vibrational motion of the bubble depends on the ratio of the velocities $\dot{V}$ and $\dot{G}$. If

$$\frac{\dot{G}}{G} \ll \frac{\dot{V}}{V},$$

then the bubble executes natural oscillations with a Minnaert frequency ν_0. To the contrary, in the case when

$$\frac{\dot{V}}{V} \ll \frac{\dot{G}}{G}$$

the motion of the bubble is aperiodic: the bubble increases or decreases in accelerated fashion, depending on the sign of the initial velocity $G_{t=0}$. In the intermediate states, when $\dot{G}/G$ and $\dot{V}/V$ are of the same order, the bubble goes through two types of motion—exponential growth (decrease) of its radius, and damped pulsations with somewhat modified frequency. The damping decrement is inversely proportional to the dimension of the bubble. If the partial pressure of the vapor is small compared with the gas pressure in the bubble, the latter will execute damped oscillations even at negligible energy dissipation.

It is undoubtedly desirable to investigate further the existing close connection between boiling and the accompanying sound.

9. BOILING OF MIXTURES AND SOLUTIONS

Physicists have been investigating the boiling of solutions for a long time, but mainly to determine the dependence of the vapor pressure on the concentration of the solution. Thus, back in 1820 Faraday deduced from his measurements that the boiling temperature of a solution is higher than that of the pure solvent. Subsequently, the results of many investigations, mainly by Babo (1847), Wellner (1860), and Tamman (1885)[43], have shown that the vapor pressure of a solvent decreases only if the solute is nonvolatile. In 1886 Raoul succeeded in finding for weak solutions of this type a simple quantitative relation: the relative decrease in the vapor pressure is equal to the concentration of the solution: $\Delta P/P = C$. From this it is easy to obtain the rise in the boiling point.

The vapor tension of liquid mixtures (i.e., solutions with volatile dissolved matter) was dealt with primarily by Konovalov[114]. The most interesting results were obtained for liquids which are miscible in arbitrary proportions (alcohol-water, chloroform-carbon tetrachloride). Konovalov established the existence of three types of mixtures. For type I (which includes the water and ethyl alcohol mixture) the vapor tension of the mixture always lies in the range $P_1 < P < P_2$ (P_1—vapor tension of water, P_2—of alcohol). P increases monotonically with increasing alcohol concentration.

For type II (for example, a mixture of water and propyl alcohol) P is always larger than either P_1 or P_2. The vapor tension reaches a maximum at a certain mixture composition. For type III (water—formic acid) P is smaller than either P_1 or P_2 and reaches a minimum at some concentration ratio. Konovalov established also the following remarkable law: the maximum and minimum vapor tensions are observed in azeotropic mixtures, for which the vapor composition coincides with the composition of the liquid phase.

During the last 15—20 years, an intense study of boiling of mixtures has begun anew, but now in connection with the accompanying heat exchange[12,113-123, 204-209,233,234].

In 1941, Bonilla and Perry[118] noted the existence, of a maximum heat transfer, considerably in excess of the heat transfer of the pure components, in a series of binary mixtures of mutually soluble liquids with certain mixture ratios. This was also confirmed by Kirchbaum[122,123], who investigated the boiling of a water-glycerine mixture. To the contrary, in two-phase systems of poorly miscible liquids the heat-transfer coefficient is lower than that of the constituents[120].

A detailed study of the boiling of different mixtures was made by Van Wijk and Van Stralen and coworkers[115-117]. A summary of their experimental results on heat transfer of boiling mixtures is given in the review[234]. Among other things, they observed the following curious fact. It turns out that the rate of boiling and the heat transfer of skimmed milk at low pressures is considerably higher than that of pure water under the same conditions. To the contrary, for some aqueous solutions there is a noticeable increase in the boiling rate compared with water at increased pressures. Numerous investigations of the boiling of mixtures of water with ketones and alcohols, and of different miscible organic substances at increased and decreased pressures, have enabled Van Stralen to draw the following conclusions concerning the critical heat transfer coefficient α_{cr}:

a) In most cases the maximum heat transfer of the mixture is much higher than that of the pure constituents. In many aqueous solutions the ratio α_{cr} (mixture)/α_{cr} (water) reaches 2 and even more. Thus, in a mixture of water with 1-pentanol methylketone this ratio is 3.5.

b) The critical heat transfer coefficient depends on the composition of the mixture. A typical curve showing the dependence of the heat transfer coefficient on the mixture composition, obtained by Van Stralen, is shown in Fig. 12. A characteristic feature of these curves is the existence of a clearly pronounced maximum at a fixed component concentration ratio. (Van Stralen observed

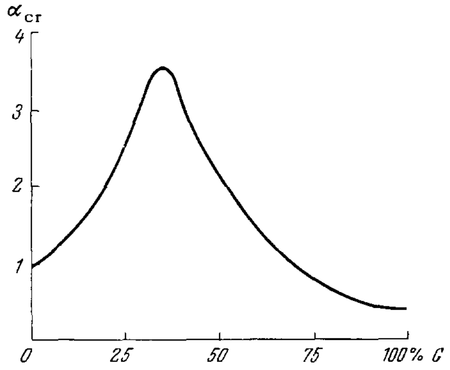

FIG. 12. Dependence of the critical coefficient of heat transfer on the composition of a mixture boiling on a thin wire.

two maxima only in several mixtures, for example water and acetone.)

A similar behavior is exhibited by binary systems whose two constituents are organic liquids. The dependence of the coefficient on the composition has in this case qualitatively the same form as for aqueous mixtures, but the maximum is less clearly pronounced. The presence of a maximum on the $q_{cr}(C)$ curve was deduced by S. S. Kutateladze, V. T. Fastovskiĭ, R. I. Artym, G. I. Bobrovich, V. N. Moskvicheva, I. I. Chernobyl'skiĭ, Yu. E. Kukach, and others[12,204,206], who investigated the dependence of the (first) critical heat flux as a function of mixture composition (Fig. 13). They also noted that the sharpness of this maximum decreases with increasing dimensions of the heated surface.

Contrary results were obtained by L. N. Grigor'ev and A. G. Usmanov[205]. They determined the coefficient α of alcohol-water and benzene-toluene mixtures as a function of the concentration for different heat fluxes.

According to their observations, α of mixtures is smaller than of pure liquids, and the $\alpha(C)$ curve has a more or less pronounced minimum at a definite mixture composition. In a later paper, reporting an investigation of heat transfer of azeotropic mixtures, these authors concluded that the curve has both a minimum and maximum, lying on two sides of the azeotropic composition. This deduction was confirmed once more by Grigor'ev in [231]. On the whole, however, the $\alpha(C)$ curve lies below the extremal point corresponding to single-component liquids.

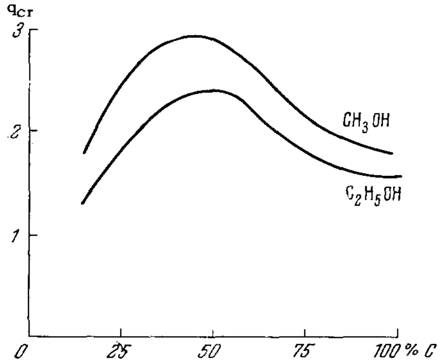

FIG. 13. Dependence of the critical heat flux on the concentration of a mixture boiling on a thin wire.

As shown by recent experiments[208,209], the observed contradiction is only illusory. The point is that in Van Stalen's experiments the mixtures were made to boil on a thin wire, while Grigor'ev and Usmanov used a tube. A special investigation was made in [208] of the influence exerted on the $\alpha(C)$ curve by the size of the heater surface and other factors. It turns out in the case of boiling on thin wires that the $q_{cr}(C)$ curve actually has a maximum exceeding by 2–2.5 times the heat flux in pure water. This maximum is particularly noticeable at low pressures (below 5 atm) and is located in the region of small concentrations of the more volatile component. With increasing external pressure, the maximum becomes less sharp and shifts towards the higher concentrations. The material of the wire does not exert a noticeable influence on the heat transfer. However, the dimensions of the heated surface are very important. Thus, when an alcohol-water mixture was made to boil not on a wire but on a plate, q_{cr} first decreased with increasing alcohol concentration, to a certain q_{min} at $C = 2–3\%$, after which it started to increase to q_{max} and $C = 15–20\%$, decreasing subsequently smoothly to values of q_{cr} of pure alcohol. q_{max} did not exceed in this case the q_{cr} of water. With increasing external pressure, the $q_{cr}(C)$ curves for either wires or plates become smoother. The same results were arrived at by the authors of [209].

Until very recently this influence of the area of the surface S of the heater on the mixture-concentration dependence of the critical heat flux q_{cr} was puzzling, since no correlation was observed between the values of q_{cr} and S for boiling pure liquids. The situation was made clearer by recent experiments by G. I. Bobrovich, I. I. Gogonin, and S. S. Kutateladze[232]. It turns out that in pure liquids that boil on a thin wire the critical heat flux also depends on the geometry of the heating surface. When the heated wire is horizontal, the heat flux q_{cr} first increases with increasing wire diameter D, reaching a maximum at a certain D*, and then begins to decrease, rapidly approaching a limiting value q^*_{cr}. For each liquid there exists a characteristic diameter of the horizontal wire, starting with which further increase of the heater wire does not influence q_{cr}. If the wire is vertical, q_{cr} exhibits no maximum, but, remaining approximately constant at large D, the heat flux q_{cr} decreases slowly for thin wires, and starting with $D \leq 0.8$ mm it drops abruptly to zero. The authors assume that the strong dependence of q_{cr} on the dimensions and orientation of the heater, which they have observed, is attributable in the case of thin wires to the difference in the conditions of evacuation of the vapor during boiling. We now can understand why the function $\alpha_{cr}(C)$ was in general more complicated than in experiments where boiling was produced on a thin wire. It is interesting to note that as the mixture composition changes the size of the bubbles detached from the hot surface also changes. The minimum bubbles are produced in a mixture with a composition that corresponds to the maximum heat transfer.

Several attempts have been made at theoretically explaining the dependence of the heat transfer coefficient on the composition of the boiling mixture. The first is due to Van Stralen[116]. Film boiling begins when the vapor bubbles start to coalesce on the hot surface into a continuous film. Therefore the smaller the average dimension of the detached bubbles and the better the liquid wets the surface, the larger the shift of the start of film boiling towards the region of higher heat fluxes.

In the case of a homogeneous system, the detached bubbles always grow on passing through a superheated liquid, but in the case of a mixture this will not always be the case. When the less volatile component evaporates in the bubble, the composition of the liquid layer surrounding the bubble becomes poorer in this component, and this increases the temperature of the phase equilibrium. It may happen therefore that an upward-floating bubble will be continuously in thermodynamic equilibrium with the mixture layer surrounding it. Such a bubble, naturally, does not grow and has minimal dimensions. According to Van Stralen, the maximum heat transfer will occur when the detached bubbles do not grow and their coagulation is difficult. It is easy to see that according to Van Stralen the maximum of heat exchange should lie in the region of low concentrations of the volatile component, for in this case the layer adjacent to the bubble is quite sensitive to the small absolute changes in its concentration.

Van Stralen's considerations are apparently highly simplified, since he does not take into account the possible occurrence of film boiling by formation of a vapor film on the heater surface itself, something that depends on the degree of wettability. In general, Van Stralen's theory, which pertains to critical heat exchange, does not take wettability into consideration. In addition, Van Stralen tacitly supposes that when the volatile substance evaporates into the bubble, only the composition of the adjacent layer changes, but not the temperature, and this certainly is not true.

Another theory pertaining to bubble boiling of mixtures was developed by Grigor'ev and Usmanov[205]. According to the Kruzhilin formula presented above (see p. 888) the radius of curvature R_0 of the smallest projection that serves as a vapor formation center is inversely proportional to the derivative dP/dT of the vapor tension with respect to the temperature. Since for mixtures the total vapor tension depends not only on the temperature but also on the concentration C, we get

$$\frac{dP}{dT} = f(T, C),$$

where the form of the function f can be determined from the Van der Waals equation for mixtures. Grigor'ev and Usmanov assume that in most mixtures f(C) has a minimum, and that R_0 has a maximum at a certain concentration C. Accordingly, the number of active centers, meaning also the heat transfer, will in this case be maximal. A somewhat different hypothesis, pertaining to the boiling of mixtures on a thin wire, was developed by the present author[214]. According to this hypothesis, the heat transfer in boiling on a wire is principally due to vapor formation. Therefore the heat given up per unit time by the incandescent filament is proportional to the rate of growth of the bubbles. The latter is in turn directly proportional to the pressure drop

$$\Delta P = P - P_0 = \frac{dP}{dT} \Delta T.$$

But dP/dT at a given temperature is a function of the concentration C, we thus conclude that $\alpha = \alpha(C)$.

Let us assume now that for a specified temperature differential ΔT the temperature gradient at the surface of the heater is small (this obviously takes place in a sufficiently thick wire or plate); the heat exchange intensity will be determined not only by the rate of vapor formation, but also by the strength of the bubbling. Therefore the connection between α and C will be less pronounced, as is indeed observed in experiment.

It must be noted that in accordance with the ideas mentioned in Sec. 8, concerning pulsating bubbles as sources of sound in a boiling liquid, the dependence of the noise intensity I(C) on the mixture composition should be similar to α(C). Indeed, measurements by V. I. Tokmakov[124] of the noise intensity of boiling alcohol-water mixtures have shown that the I(C) curve has a pronounced maximum in the region of small alcohol concentrations. E. V. Lykov[125] confirmed this conclusion for a broader class of mixtures and observed an undisputed parallelism between the functions I(C) and α(C).

The analysis of the kinetics of boiling of solutions and mixtures has not received its due attention. The first known attempt to determine the rate of condensation in supersaturated vapor of a mixture of two liquids was made by Flud[51a]. Although Flud did not take into account in his theory the dependence of the surface tension on the composition of the drop, the agreement with experiment is perfectly satisfactory. In 1940 Doring and Neimann[127,126] reported on investigations of the condensation of a mixture of vapors, with allowance for the influence of the concentrations and the curvature of the drop on the adsorption and the surface-tension coefficient. This has led to better agreement between the calculations and Flud's experimental data.

The kinetics of boiling of solutions of gases in a liquid medium was considered theoretically in [54,128].

The main deductions of these investigations can be readily generalized to the case of boiling of arbitrary mixtures.

It turns out that the rate of boiling of a mixture depends principally on the total vapor tension of the two components, and not on the ratio between the partial tensions.

The critical nucleus, i.e., the bubble which is in mechanical and thermodynamic equilibrium with the mixture, is now characterized not only by its radius, but also by its composition. However, even for a mixture one can speak in practice of a bubble of critical size R*, above which any bubble will have a tendency to grow.

When the volume of the nucleus changes its composition, generally speaking, also changes, but the decisive influence on the "fate" of the bubble is exerted as before by its dimension. This is clearly seen from Fig. 14. The axes represent the numbers of molecules of each component in the bubble. The curves with the arrows represent the "streamlines" of the bubbles.

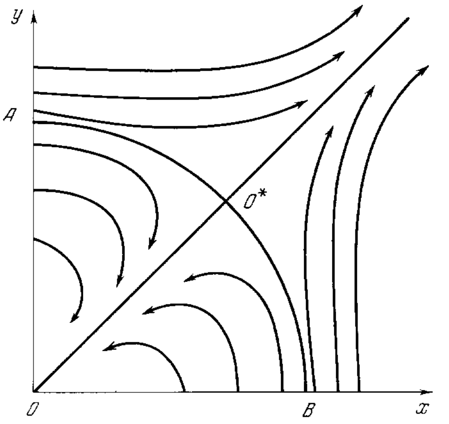

FIG. 14. Character of change of bubbles in a superheated mixture. x, y – number of molecules of first and second components; the line OO* corresponds to thermodynamic equilibrium of the bubble; the line AO*B is the geometric locus of the critical nuclei; the arrows show the "current lines" of the bubbles.

The critical line AO*B represents the aggregate of the bubbles of critical size, dimensions. The ratio y/x, which is determined from the equation of the line OO*, characterizes the composition of the bubbles that are in thermodynamic equilibrium with the solution. The boiling of binary solutions is discussed also in [210-213].

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