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BOILING OF BINARY MIXTURES—STUDY OF INDIVIDUAL BUBBLES

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Abstract—Experiments are reported in which individual bubbles of vapour are grown at a plane wall in initially stagnant isothermal liquid. Such tests had already been done and satisfactorily analysed and understood for pure liquids, but here the liquids are binary mixtures of hexane and octane of varying composition.

The chief result is that ciné observations of the general behaviour of such bubbles (rate of growth, change of shape, time and size at departure) presents no new problems; it is identical to behaviour in pure liquids, provided one change of parameter is made. That change is to substitute the correct temperature for the evaporating binary interface in place of the saturation temperature for the pure liquid. That interface temperature was determined by reference to recent analytic solutions for evaporation of semi-infinite binary liquid by diffusion of heat and mass.

Detailed rapid thermometric observations were also made, of the temperatures at the wall below the bubble and inside the bubble. They showed some aspects which differ markedly from pure liquids (though not such as to affect general behaviour). Those aspects were explained by detailed analysis of diffusion of heat and mass in a thin layer of liquid (microlayer) left beneath the growing bubble.

Implications for boiling heat transfer are also considered, and it is shown that this analysis of individual bubbles does not, of itself, explain the known reduction in heat transfer coefficient between pure and binary liquids. Several existing methods of explaining that reduction are examined and shown to have a common basis close to that determined by our analysis of single bubbles. But on extending from that basis in a simple way, to predict boiling heat transfer rates, they fail, except where an additional pressure-dependent multiplier is introduced, on purely empirical grounds.

NOMENCLATURE

A,	surface area of bubble;
b,	growth parameter $(dV/dt)/(A/\sqrt{t})$;
c_p,	specific heat capacity;
D,	bubble dimension (Fig. 4);
D,	diffusion coefficient;
F,	function defined in Appendix 2;
g,	acceleration of gravity;
$g(w)$,	function defined in Appendix 1;
G^+,	Gibbs' function (Appendix 2);
h_{fg},	enthalpy change of evaporation;
h_i, h_{BL},	surface heat transfer coefficients;
h,	thickness of microlayer;
H,	bubble dimension (Fig. 4);
Ja,	Jakob number $(\rho_f/\rho_g)c_p(T_D - T_e)/h_{fg}$;
k,	thermal conductivity;
K,	parameter in Appendix 1;
p,	pressure;
Pr,	Prandtl number ν/α;
$(\dot{q}/A)$,	heat flux rate per unit area;
Sc,	Schmidt number ν/D;
t,	time;
T,	temperature;
V,	volume of bubble;
x,	molar fraction in mixture;
z,	distance.

Greek symbols

α,	thermal diffusivity;
ρ,	density;
σ,	surface tension;
ν,	kinematic viscosity.

Subscripts

B,	limiting case (Fig. 1);
BL,	bubble line;
D,	T_D driving temperature; t_D departure time;
e,	evaporation;
f,	liquid;
g,	gas;
g,	in t_g: growth time;
i,	interface;
l,	liquid;
LV,	less volatile;
0,	initial (local);
sat,	saturation;
v,	vapour;
vY,	vapour at height Y;
w,	wall;
∞,	initial (extending to infinity).

INTRODUCTION

MANY INDUSTRIAL processes involve boiling of mixtures and this problem has been widely studied, generally with a view to measuring, and if possible predicting, heat transfer coefficients. Such coefficients are hard to predict even for pure fluids and they are very sensitive to changes of parameters. Therefore a frequent approach to binary boiling has been to consider a series of tests of steady boiling, with varying composition from one pure fluid to the other, while keeping constant many other conditions of the test—the geometry, material and surface of the heater. It is then customary to define a heat transfer coefficient as $(\dot{q}/A)/(T_D - T_{BL})$, where T_D is the driving temperature (usually heater temperature) and T_{BL} is the bubble line temperature as shown in Fig. 1, a constant pressure equilibrium diagram for a typical binary mixture not forming an azeotrope. The heat transfer coefficient so defined will here be designated h_{BL} and it has generally been found that, at a given system pressure and given heat flux rate $(\dot{q}/A)$, h_{BL} varies with molar composition broadly as indicated in Fig. 2.

This phenomenon has been known for some time, and various analyses have been applied, based on the recognition that the driving potential $(T_D - T_{BL})$ is not fully available for inducing heat diffusion, as there must be mass diffusion as well. The vapour generated by boiling a binary mixture is richer in the more volatile component than the original bulk liquid. Hence, when evaporation occurs it causes the remaining liquid to become depleted in the more volatile component. Consequently, that component diffuses towards the evaporating interface and the less volatile component diffuses away from it. In a sufficiently simple situation, a double diffusion problem of this kind has an analytic self-similar solution, and that is quoted here as a useful reference case. It refers to the evaporation from the plane surface of a semi-infinite mass of binary liquid at constant pressure and initially of molar composition x_∞, temperature T_∞, where T_∞ takes the place of T_D and is greater than T_{BL}. Appendix 1 shows the initial conditions, the equations of diffusion of heat and mass, and the interface conditions (including rate of movement of interface consistent with both heat diffusion and mass diffusion), all of which are satisfied by appropriate error functions for x and T. That solution proves that, at the interface, the temperature T_i, and compositions x_{li} of the liquid and x_{vi} of the vapour all have constant values, determined as indicated in Appendix 1. The driving potential $(T_\infty - T_{BL})$ can indeed be regarded as split into two parts: $(T_\infty - T_i)$ available for heat diffusion, and $(T_i - T_{BL})$ required for mass diffusion.

A similar argument applies to a spherical bubble, provided it is diffusion controlled and the thicknesses of the boundary layers of temperature and composition are much less than the radius (an asymptotic case of a general argument by Scriven [1]). It has also been shown by van Ouwekerk [2] that the same argument applies to a diffusion controlled bubble growing at a wall, provided that effects of surface tension are small, so that the bubble retains a self-similar (nearly hemispherical) shape. In many industrial applications, and in the present experiments, the bubbles were diffusion controlled for virtually all of their observed life. That means that the excess of the pressure in the bubble over the system pressure at infinity (required to drive the fluid motion) was small in the sense that its effect on saturation or equilibrium temperature was much less than the driving temperature difference $(T_D - T_i)$. The equilibrium diagram (Fig. 1) at system pressure could therefore be taken to apply to the bubble interface at all times. The contrary case, inertia control, and the transition from inertia control to diffusion control have been much analysed for pure liquids [3, 4].

This might suggest that, in binary boiling, the heat flow rate is more likely to be dependent on $(T_D - T_i)$ than on $(T_D - T_{BL})$. If so, then tests of the type described in Fig. 2 should be considered in terms of a different heat transfer coefficient, $h_i = (\dot{q}/A)/(T_D - T_i)$. Since T_i is rather awkward to determine (and indeed the very existence of that solution has not long been known), many alternative approaches have been proposed. They can now be seen either as ways of determining T_i or as ways of reducing $(T_D - T_{BL})$ to an "effective" value, to account for mass diffusion. They use linearisations and other approximations which are generally more or less accurate as they become less or more convenient. Some of these approaches are summarised in Appendices 1 and 2, where it is shown that, with high superheat, they can lead to predictions of T_i above the condensation line, which is impossible. However, in many studies of bubble growth and boiling heat transfer, the differences among predictions are swamped by scatter in the data, and other effects.

These methods all have a broadly similar effect, of producing a curve for h_i in Fig. 2 which lies everywhere above h_{BL}. The broad dip is therefore reduced, in some cases eliminated. In an effort to match the observed dip, one of the approaches ([5] and Appendix 2) introduces an empirical constant to increase the amount of driving potential "lost" to mass diffusion or

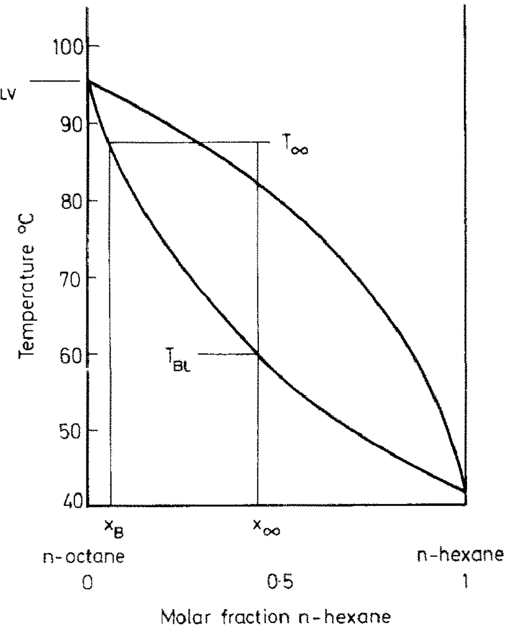

Fig. 1. Equilibrium diagram for *n*-hexane and *n*-octane at 300 mm Hg pressure.

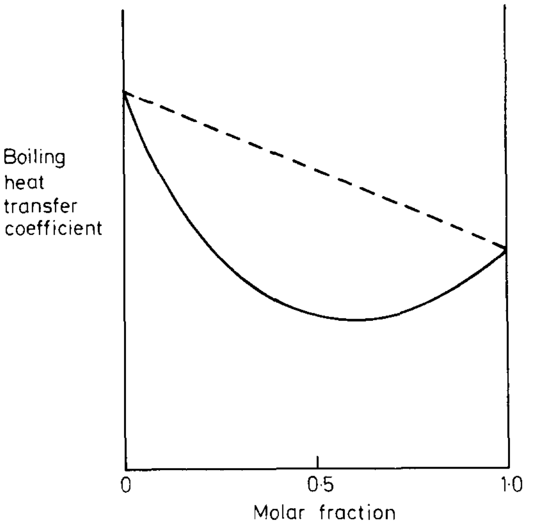

FIG. 2. Typical variation of boiling heat transfer coefficient for a mixture; tests at constant pressure and heat flux rate.

to nucleation. However, that approach was not entirely satisfactory as it was not possible to give any theoretical basis for that constant and it had to be determined empirically for every pair of fluids considered.

Thus it appears that the substitution of T_i for T_{BL} may be a significant advance but not the complete key to the binary boiling problem.

Another factor is that the properties of the fluid depend on composition, perhaps in a non-linear way. Such properties (particularly mass diffusivity, D) may be very difficult to establish, but the indications are that allowing for property variation will not explain the remaining discrepancy. It can be useful to conduct tests with mixtures of two fluids belonging to the same homologous series, but having significantly different boiling points. For such fluids, the other properties (ρ, k, c_p, h_{fg}, D, etc.) will be similar, and these properties for mixtures will also be reasonably similar and predictable. Such mixtures may still show an appreciable dip in the h_i/composition curve, which cannot now be attributed to variation of properties.

A further class of phenomenon which is related to diffusion rates through evaporation rates, concerns bubble behaviour, principally rate of growth, shape and time and size at departure. Variations in these may be induced by the variation in driving potential and thus "amplify" the effect on heat flow.

There may be highly significant effects from other phenomena which are not closely related, such as those involved in nucleation, which affect the waiting time and the density of nucleation sites per unit area of the heater. As discussed in Appendix 2, nucleation is addressed in [5].

Aims of the present study

In this situation it is possible to make a contribution, which may be small but useful, by providing firm data about the behaviour of individual bubbles grown at a wall in a binary mixture. The data could confirm (or deny) the theories above, in so far as they predict or have implications for the behaviour of such bubbles. A series of tests was therefore carried out with individual bubbles grown under closely controlled conditions—basically growth into initially stagnant isothermal binary liquid. These were compared with results from previously reported experiments with similarly controlled growth into pure liquid, with and without gravity [6]. Broadly it was found that binary bubbles did behave very much as predicted by the theory above, in fact, if T_{sat} of the pure liquid is replaced by T_i, then the bubble behaviour appears almost identical. That statement applies throughout their life at the wall and includes their rate of growth, their change of shape and their time and size at departure. In more detail, observations were made of transient temperature variations inside the bubble and at the wall beneath it. These were significantly different from observations of similar quantities in pure liquids. Although these differences have little effect on overall bubble behaviour, as stated above, the differences were examined and explained. As they do not appear crucial for boiling, the differences were not pursued to high accuracy. They were explained by straightforward consideration of combined diffusion of heat and mass in the binary liquid layer (microlayer) beneath the bubble, which is thin, so the self-similar solution for semi-infinite liquid does not long apply.

DESIGN OF EXPERIMENT

Fluids and composition

In order to show-up differences from the pure liquid, experimental conditions were chosen which were expected to produce recognisable differences in behaviour which could then be ascribed to known causes. In order to avoid difficulty with determination of mixture properties, it was decided to use *n*-octane and *n*-hexane which have significantly different boiling points (126 and 69°C at 1 atm) but belong to the same homologous series so that their other properties do not differ greatly (e.g. latent heat 330 and 320 kJ/kg) hence interpolation for properties of the mixtures would be less likely to introduce uncertainties. Having removed that source of difference from pure liquids, the operating conditions were then chosen to emphasise the other source of difference, namely the difference between T_{BL} and T_i (Fig. 3). Preliminary calculation for that mixture, summarised in Appendix 1, suggested that, for mixtures in the range 10–50% hexane, the ratio of temperature differences $(T_\infty - T_i):(T_\infty - T_{BL})$ would be of order 0.7:1 and should produce observable effects. The low electrical conductivity of the fluids was also advantageous, permitting the use of electrical circuits in contact with the liquid, as described below.

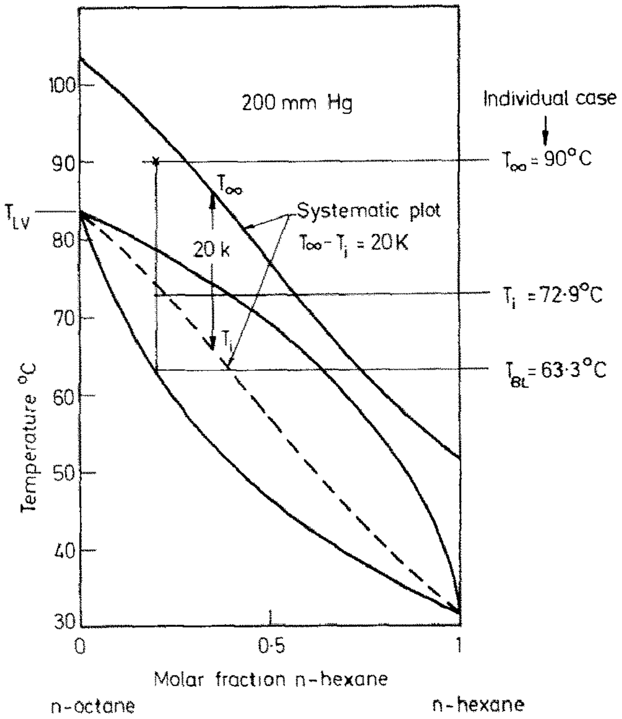

Fig. 3. Equilibrium diagram, showing interface temperature T_i and its variation from T_{BL}.

Apparatus and operation

As in the experiments with pure liquid [6], a jacketed test vessel (Fig. 4) was used to produce the required initial conditions of isothermal stagnant liquid. The jacket had flat glass sides to facilitate observation and contained heavy paraffin, heated by a controlled supply to an electric kettle element. The inner vessel was an inverted bell jar containing the test fluid, in which the initial temperature could be measured and checked for spatial uniformity by a mercury in glass thermometer or a moveable thermocouple. A glass plate was mounted horizontally towards the bottom of the test fluid and thin film circuits on the top surface of the plate acted as small high-speed resistance thermometers, as described in [6, 7]. Thermocouples made from 30 μm dia. wire were mounted in chosen positions a few millimetres above the plate. Their junctions were made using micromanipulator and binocular microscope, with a d.c. supply of 20 V, both wires being anodes and a carbon block being the cathode, as described in [8]. A typical junction was approximately spherical, some 40 μm dia. Pressure at the top of the vessel was measured by mercury manometer and also, for rapid variations, by a pressure transducer and galvanometer, with frequency response to 1.6 kHz.

In a typical experiment, the apparatus was gently heated to slightly above the intended initial temperature, then allowed to settle, cool slightly, and stabilise. Pressure, hitherto above the corresponding "saturation" value, was then lowered to below "saturation". Provided the system had been thoroughly cleared of unwanted nucleation sites, this super-saturated state could be maintained for some seconds, though evaporation from the top of the liquid caused rapid local cooling there, and downward convection "fingers" of cold liquid formed quickly. In the few seconds before those "fingers" reached the test zone, a bubble was initiated at the test plate by passing a brief current pulse through one of the thin film circuits, used as a bubble trigger instead of as a thermometer. In many cases, a second bubble was triggered at a predetermined interval after the first, in order to observe how such a bubble was affected by its predecessor. Since there were few data available on these pairs of bubbles in pure liquids, tests of this type were first done in pure hexane and pure octane. The lights, high-speed camera and high-speed recorder were in operation for a second or so before and after the bubbles. More details of the techniques, including the frequent calibrations, are given in [8]. Effects of errors are discussed in [8].

RESULTS

In acdition to initial readings of thermometers and manometers, results were obtained as high-speed movies and u.v. recordings of variation in electrical signals from the resistance thermometers, thermocouples and pressure transducer. These will be considered in turn.

High-speed movies

Movies were normally taken at 500 frames/s and some 400 runs were analysed in detail. An analytical,

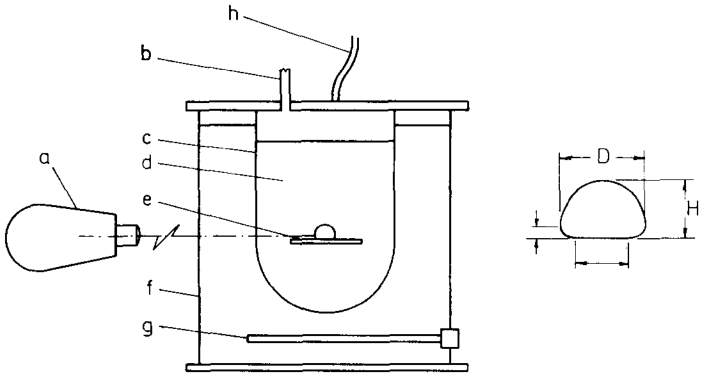

FIG. 4. Sketch of experimental apparatus and bubble measurements. (a) camera; (b) connection to condenser; (c) inner vessel; (d) test liquid; (e) test plate; (f) outer jacket; (g) jacket heater; (h) electrical connections.

frame-by-frame projector was used, giving an image about 6 times life size (determined accurately by test patterns), on which measurements were taken to 1 mm, though the bubble profile could not always be positively located to that accuracy. Four key measurements were taken on each frame before departure, as indicated in Figure 4, from which the volume V and surface area A could be calculated, assuming axial symmetry and regarding the upper and lower sections as semi-ellipsoids, the lower being truncated by the wall. From those data it was possible to determine whether or not the bubble conformed to the pattern for growth which had been observed [6] to apply for bubbles in pure liquids which were isothermal and stagnant. That pattern is very simple and useful, and it was first reported in [6], where it was shown to enable a powerful dimensional analysis to understand bubble growth in pure liquids, described briefly below. The pattern is

$$\frac{\mathrm{d}V/\mathrm{d}t}{A} = \frac{b}{\sqrt{t}}$$

or

$$V = \int A \times \frac{b}{\sqrt{t}}\,\mathrm{d}t, \quad b = \frac{V}{\int \frac{A}{\sqrt{t}}\,\mathrm{d}t},$$

where b is a constant for each bubble and had been found to be slightly over $Ja\sqrt{\alpha}$, typically 1.1 $Ja\sqrt{\alpha}$. It should be noted that the area A includes the area below the bubble. The integrated form is less affected by the inevitable error in measurement on successive frames of the movie, and the present results were processed in that way. It was apparent that bubbles in binary mixtures were growing in much the same way as in pure liquids and the constant b should again take the value 1.1 $Ja\sqrt{\alpha}$, provided the temperature difference in Ja was taken to be $(T_\infty - T_i)$. Thus, for bubble growth, the temperature T_i takes the place of T_{sat} for a pure liquid. This point is illustrated by Table 1, which summarises our data in the form of the ratio $b/(Ja\sqrt{\alpha})$. Items in that table give averages and standard deviations of that ratio, in five columns corresponding to pure octane, pure hexane and the three mixtures we used.

The table includes all readings of this type excepting those on two days (just after raising operating temperature from 80 to 90°C) when the pressure calibrations before and after the day's work did not match, and in addition, three further tests, all with pure liquid and a high value of anticipated error, as shown by error analysis [8].

Dimensional analysis

We can therefore argue for binary liquids, as for pure liquids [6] that the quantity b is the only information required from the energy equation. Having thus decoupled the energy equation from the fluid mechanics, we are left with b and a fluid mechanics problem. Hence any observed quantity X must depend only on b, time and properties relevant to fluid mechanics, so $X = f(b, \rho, \mu, \sigma, g, t)$. Hence any dimensionless variable such as the ratio D/H or $D^* = D/(b\sqrt{t})$ must be a function of 3 dimensionless groups, conveniently taken to be a dimensionless time independent of viscosity, $t^* = t/(b^6\rho^2/\sigma^2)$, dimensionless gravity $g^* = gb^8\rho^3/\sigma^3$ and the group $b/\sqrt{\nu} = Ja/\sqrt{Pr}$. The last seems to have little effect on overall shape (though affecting the microlayer). These arguments were first established in [6], where quantities such as D/H and D^* were first examined and understood in the simpler environment of zero gravity (free fall). Then gravity was re-introduced and the combined effect could be readily understood as a one-parameter variant of the simpler zero g case. The work reported in [6] used pure liquids. Since the present work on binary liquids also showed that simple growth pattern with $b = Ja\sqrt{\alpha}$ (with appropriate temperature differ-

Table 1. Values of ratio $b/(Ja\sqrt{\alpha})$

	Pure octane	Mixtures Molar fraction of octane 0.9	0.75	0.5	Pure hexane
Number of tests	17	31	74	29	82
Average value	1.05	1.12	1.07	1.05	1.13
Standard deviation	0.15	0.07	0.06	0.05	0.06

ence in Ja), the same arguments apply. The quantity b is the only information required from the energy and composition equations, and we are again left with b and a fluid mechanics problem. Dimensional analysis leads to similar predictions of dependence on t^* and g^*.

These predictions were borne out by the present experiments. The ratio D/H is evaluated here, as it was in [6], because it is a good general indicator of change of shape, varying from 2 to 1 as the bubble shape changes from hemispherical to spherical, but unfortunately it amplifies truncation errors in measurement, which cause appreciable scatter, particularly at small sizes. The first few frames of each bubble must be discarded on those grounds, and also because the effects of artificial nucleation of bubbles may still be present, sometimes in the form of oscillations. Later frames, whether referring to pure hexane or octane or their mixtures, all show the same behaviour as indicated in Fig. 5. The full line there shows the variation of D/H with t^* in zero gravity, established in [6]. Gravity causes D/H to fall below that line, ending with departure at time t_D^*, clearly related to g^*. The fine thermocouples caused little perturbation in this overall bubble behaviour.

A knowledge of departure time is of importance in many correlations for heat transfer rates in boiling, and Fig. 6 shows the relation between t_D^* and g^*, as first established in [6]. Against the data for pure fluids from [6] are indistinguishable from the new data for pure fluids and for mixtures.

Hence all the major characteristics of growth, change of shape and departure under gravity are readily explained in terms of previous work [6], provided the driving temperature difference is reduced from $(T_w - T_{BL})$ to $(T_w - T_i)$, as predicted by simple application of the self-similar solution of Appendix 1.

High-speed thermometry—temperature of wall

In our first tests with binary liquid, the response of the thin film resistance thermometers on the surface of the test plate was soon seen to differ from that for pure liquids. Two typical tests with pure liquid are shown in Fig. 7(a), and one for binary mixture in Fig. 7(b). It seemed likely that the hydrodynamic forces which caused a thin layer of liquid (microlayer) to form below the bubble in a pure liquid would apply equally here. However, the microlayer was having different effects on wall temperature, which could not be handled by simply substituting T_i in binary liquid for T_{sat} in pure liquid—a method which might be expected to explain differences if the situation was dominated by the self-

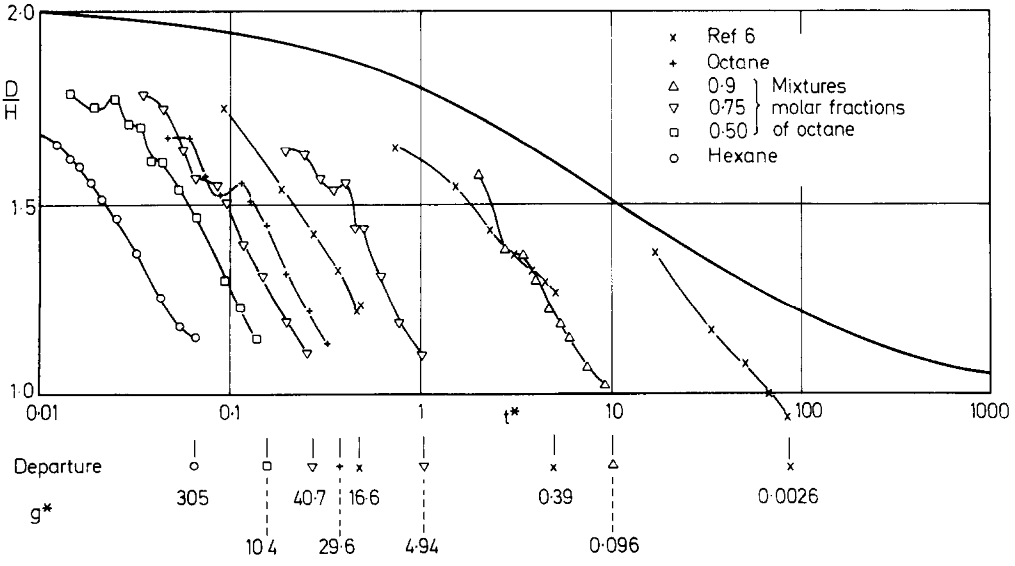

FIG. 5. Change of shape of bubbles, indicated by D/H, as a function of t^* and g^*.

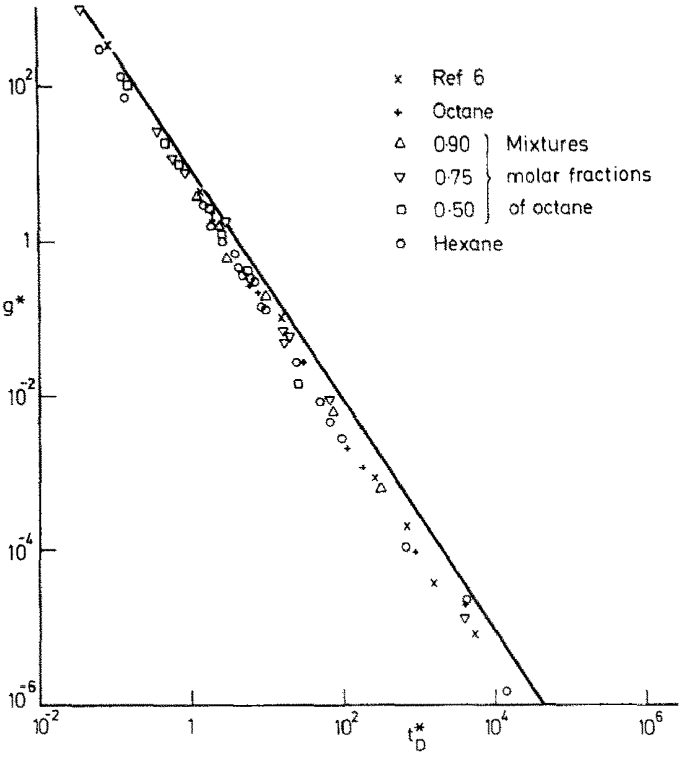

FIG. 6. Departure of bubbles—relation between t_D^* and g^*.

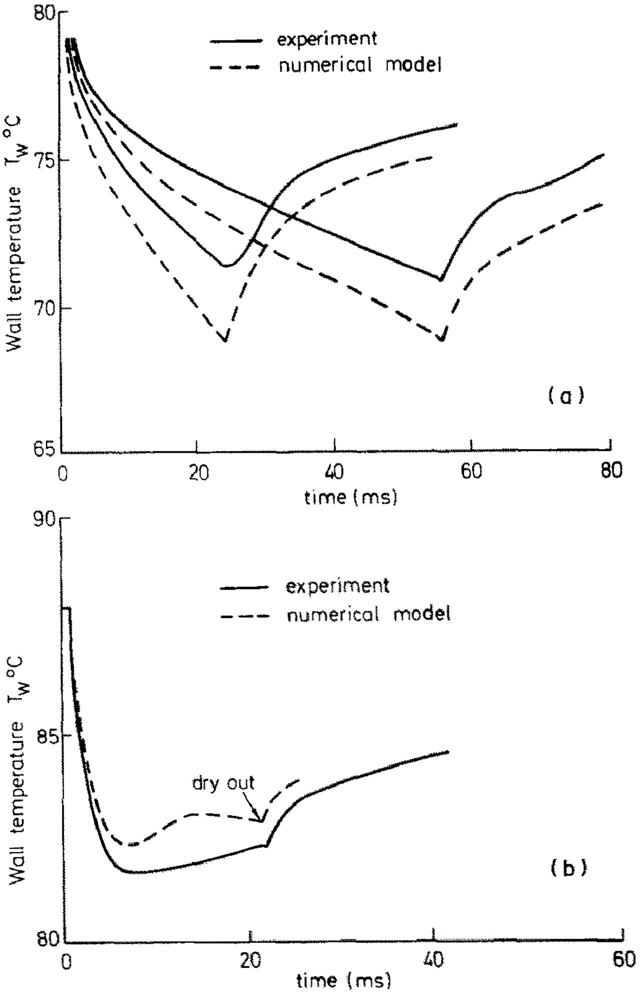

FIG. 7. Variation of wall temperature below bubbles (a) two tests with pure liquid; (b) one test with binary mixture.

similar solution of Appendix 1. However, that self-similar solution applies to a semi-infinite mass of liquid whereas the wall temperature in question is dependent on phenomena in the thin microlayer, principally thermal diffusion and depletion of the volatile component, as will now be discussed.

The initial thickness h_0 of a microlayer is of order $\sqrt{(\nu t_g)}$, where t_g is the time for the bubble to grow to the point concerned: typically, h_0 is 10–20 μm. For times much shorter than h_0^2/α $(=Pr\, t_g)$ such a layer can be regarded as infinitely thick, in the sense that phenomena at the top of it are unaffected by the thermal properties of the wall. As time approaches h_0^2/α, the thermal properties of the wall affect the temperature field at the wall and after a further such time, that effect diffuses back to the evaporating surface and affects rate of evaporation. So far, the argument applies equally to pure or binary liquids. However, the effect on that evaporation rate is more complex for binary liquids, since the composition at the evaporating interface can vary. Hence T_e, the temperature of evaporation, varies. It rises if the wall has a higher value of $(k\rho c_p)$ than the liquid. An additional effect arises in binary liquids when, after a time of order h_0^2/D $(=Sc\, t_g$, usually considerably greater than $Pr\, t_g)$, the mass diffusion field is affected by the wall, where there is of course a zero-flow boundary. Thereafter the microlayer will be progressively depleted in volatile component. Two cases arise:

(a) If the initial temperature T_∞ exceeds the boiling point T_{LV} of the less volatile component at the prevailing pressure, then the temperature of the evaporating interface can rise to T_{LV} and eventually the whole microlayer may evaporate away.

(b) If T_∞ is less than T_{LV}, then the composition of the microlayer can never go beyond x_B on Fig. 1, and the microlayer cannot evaporate completely.

To follow these phenomena, we set up and com-

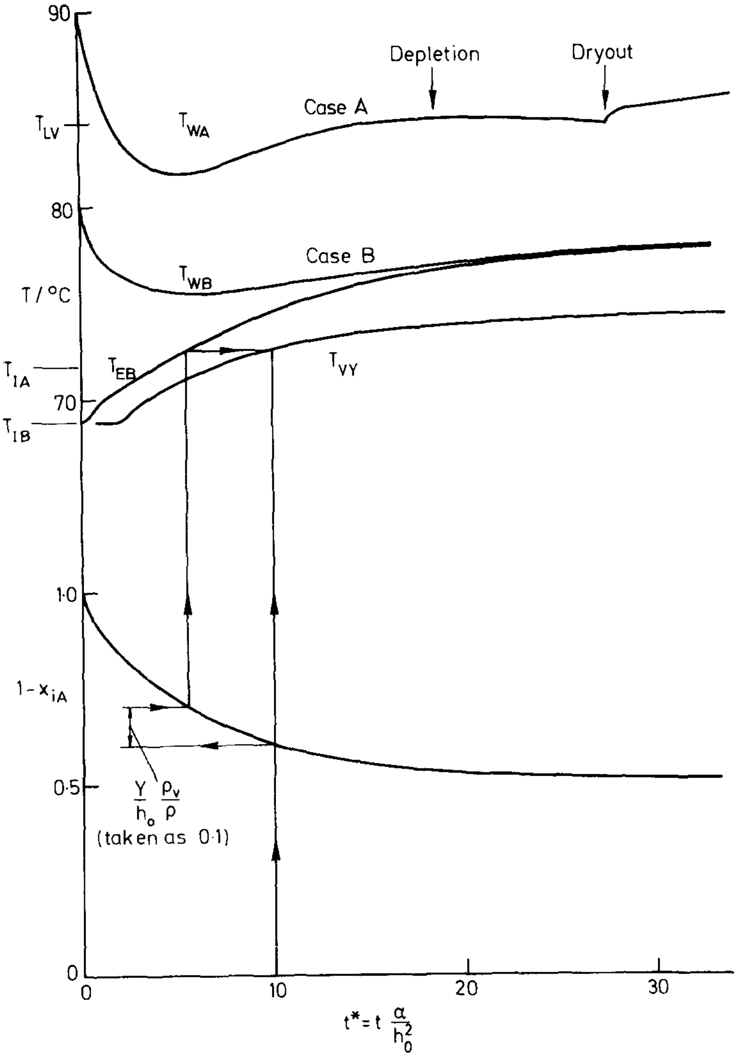

FIG. 8. Computed prediction of composition and temperature from evaporating binary microlayer. Case A: T_∞ exceeds T_{LV}. Case B: T_∞ below T_{LV}.

puted a 1-dim. model with a layer of evaporating, depleting binary liquid overlying a solid wall of different thermal properties, as described in [8, 9]. Typical results for the two cases (a) and (b) are given in Fig. 8. In neither case does the wall temperature T_w fall to T_i. Instead it falls in each case to a minimum, well above T_i, and then rises steadily as the microlayer is depleted in volatile component and the temperature T_e at the evaporating interface rises correspondingly. In case (a), dryout eventually occurs and the wall temperature rises more quickly thereafter. As shown in Fig. 7(b), these computed results are in general accordance with the experimental observations, thus confirming that there is a microlayer of about the thickness expected for pure liquids, and that its evaporation is naturally affected by mass diffusion as well as thermal diffusion but shows no new physical phenomenon.

High-speed thermometry—temperature in bubble

In tests with binary mixtures, high-speed thermometry was extended to measurement of temperatures in the vapour. Fine thermocouples were made as described earlier, because it was realised that such measurements would need a sensor of small size and small thermal capacity. They were mounted as shown in Fig. 9, and after the bubble had grown past a thermocouple, its reading changed in various ways. The observed temperature first fell close to T_i but then rose steadily, possibly interrupted by a smaller second sharp fall. The first fall and subsequent rise will be seen to be consistent with the computation reported above, when it is recognised that the thermocouple will be exposed to vapour coming past it at various compositions and temperatures. The first vapour to surround it will be that from the curved surface of the bubble or from newly formed microlayer, both of which would be at approx. T_i. Later, it would be surrounded by vapour evaporated at a later stage from the microlayer below it. If we assume that vapour travels in a "column" normally away from the microlayer at the rate dictated by subsequent production of fresh vapour below it, then we can determine when the vapour reaching the thermocouple would be at temperature different from T_i due to the effects analysed above. In fact the construction sketched on Fig. 8 shows how we can determine the original composition and temperature T_{vY} of the vapour currently reaching a thermocouple placed at height Y above the wall. If diffusion in the vapour is neglected then that vapour would still be at its original temperature. As shown in Fig. 9, that construction does predict the general trend of the thermocouple observation. The actual response of the thermocouple depends further on its own thermal capacity and the coupling (heat transfer coefficient) between vapour and thermocouple, which in turn depends on whether the junction was left wet or dry as the liquid departed from it (a matter very hard to examine by direct observation). Some of these factors would have significant effects on thermocouple temperature, including certain qualitative aspects, such as

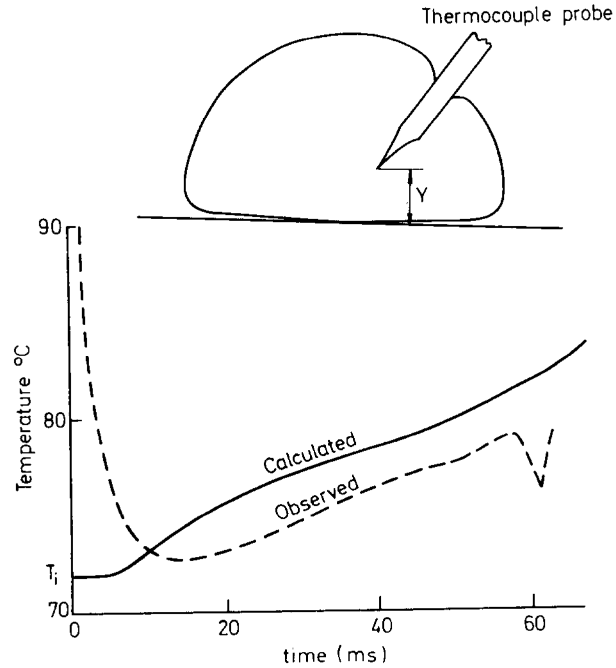

FIG. 9. Small thermocouple probe, position and typical readings, compared with theoretical prediction, based on Fig. 8.

the second sharp fall after the initial fall.

There is a tendency for the rise in temperature to accelerate as the bubble departs, which may be due to the "column" moving bodily upwards towards the thermocouple due to the motion of the bubble. The subsequent sharp fall is presumably due to encountering liquid in a cooler layer just around the bubble. The analysis is therefore not complete, but the general trends confirm a model of evaporation from the microlayer as computed above, and from the curved surface of the bubble in accordance with the self-similar solution of Appendix 1. The matter was not pursued further, as it was felt to be peripheral to the main issue of boiling, for which the results on overall bubble behaviour are of prime concern.

There may appear to be an inconsistency above, because the overall growth of the bubble is in accordance with the self-similar solution of Appendix 1, while the detailed temperature readings discussed above are not in accordance with that solution. The discrepancy is resolved here, as for pure liquid, by noting that the sources of the majority of the vapour for bubble growth are the curved surface of the bubble and the outer regions of the microlayer. For those sources, evaporation is governed by the self-similar solution, with modification for the radial growth, also self-similar, as discussed in [10]. The divergences from self-similarity arise from behaviour in the microlayer after times which are long compared with growth time, hence that behaviour is confined to a relatively small region near the centre of the microlayer, making relatively little contribution to vapour production. There is an element of self-cancellation, as the wall is usually more conducting than the liquid, hence increasing vapour production, but the vapour production slows down as the microlayer approaches dry-out or full depletion in volatile component, as shown in Fig. 8. The matter has been analysed for pure liquids [10, 11] and for binary mixtures [8].

IMPLICATIONS FOR BOILING

Use of T_i

The observations discussed above confirm that, in a binary liquid, the growth and departure of reasonably fast-growing diffusion controlled bubbles is governed by T_i, in the sense that the results for pure liquid could be carried over to binary mixtures by substituting T_i in place of T_{sat}. If we consider the hypothesis that boiling is purely governed by bubble behaviour, then boiling would also be governed by T_i in the same sense. Tests of steady boiling as discussed in the introduction and shown in Fig. 2 are useful here as they incorporate results from pure liquids at the two ends of their range. Hence that hypothesis would suggest that if we use $h_i = (\dot{q}/A)/(T_D - T_i)$ instead of the conventional $h_{BL} = (\dot{q}/A)/(T_D - T_{BL})$ the results should fall into a simple pattern, varying between the two pure liquids, in a way determined by the variation of properties. If the two pure liquids are similar and their properties do not differ greatly, then the properties of the mixture should be close to those of the pure liquids, related to them approximately by a linear function of composition. The variation of h_i would then be a linear function of composition.

This series of hypotheses can be tested by taking published data of h_{BL} for tests of this kind, and processing the results to recover T_D, and hence obtain T_i, hence h_i.

That has been done, in particular, for the results of Stefan and Körner [5], taking further details from [12], with the help of discussions with Professor Stefan. Two key figures from [5] are partly reproduced here as the full lines in Figs. 10(a, b). They refer to tests under experimental conditions which were constant except for composition, which varied from pure acetone to pure *n*-butanol. Also, they refer to tests in which the heat flux ($\dot{q}/A$) was $10^5\,W/m^2$. The heat transfer coefficient plotted in Fig. 10(b) was $(\dot{q}/A)/(T_D - T_{BL})$, so we can recover $(T_D - T_{BL})$, from Fig. 10(b), and hence T_D by taking T_{BL} from Fig. 10(a). By further use of Fig. 10(a), in accordance with Appendix 1, we determine T_i, hence h_i. The resulting values of T_D, T_i and h_i are shown as dotted lines in Figs. 10(a, b). There is some uncertainty about properties of the mixtures, particularly mass diffusivity D, particularly at the higher pressure (10 atm.) which corresponds to reduced pressure (p/p_{crit}) of 0.218 for acetone and 0.232 for *n*-butanol. Also the equilibrium diagrams of Fig. 10(a) differ by a few degrees from published data for the fluids involved. Nevertheless, a clear trend can be seen, that h_i is almost linearly dependent on x for the results at 1 atm, but not for the results at 10 atm. The non-linearity in the latter case seems more than could be caused by the uncertainty in the properties or non-ideality of the fluids.

Hence the various hypotheses above do not represent steady boiling completely. A tentative result from these two tests is that, although steady boiling of these fluids at 1 atm may be largely governed by bubble behaviour, it is not so at 10 atm. That result is already implied in the empirical correlation of Stefan and Körner [5], discussed in Appendix 2. In effect, they used an argument from nucleation to produce ΔT_E, an approximate counterpart of $(T_i - T_{BL})$, and they then found that, to fit their results, they needed a universal empirical dependence on pressure $(0.88 + 0.12\,p)$ with p in bar, as well as an empirical constant of order 1, differing for each pair of liquids (1.18 for this pair).

CONCLUSIONS

Individual bubbles of vapour were grown under carefully controlled conditions at a plane wall in binary liquid, initially stagnant and of uniform composition and uniform (supersaturated) temperature. Their rate of growth, change of shape and departure were observed and found to conform closely to behaviour observed in pure liquid, provided an interface temperature was determined and regarded as

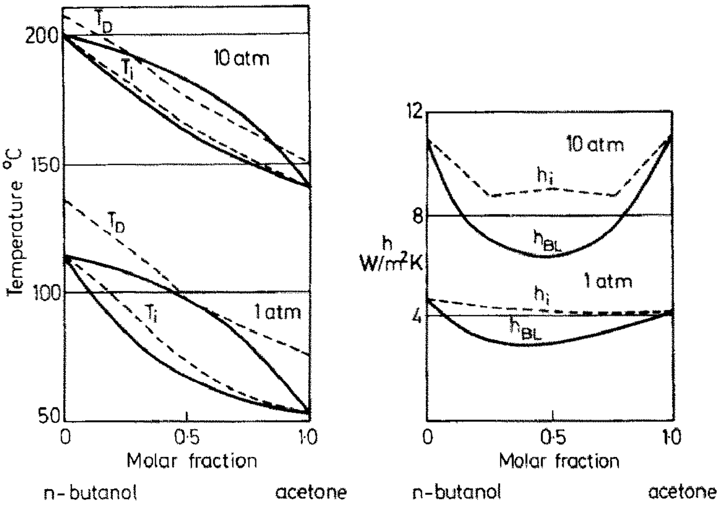

FIG. 10. Experimental results of [12] re-processed to determine h_i in place of h_{BL}. (a) Equilibrium diagram and deduced T_D, T_i; (b) variation of heat transfer coefficients h_i, h_{BL} with molar fraction.

replacing the saturation temperature of a pure liquid. The value of that interface temperature was determined from the exact self-similar solution for diffusion of heat and mass in one dimension. Our predictions for behaviour of binary bubbles are better than those derivable from other analyses which have been proposed for making effective allowance for mass diffusion. Those employed a broadly similar approach, but used various linearisations and approximations which would lead to manifestly incorrect solutions in some cases.

When applied to heat transfer coefficients in developed boiling, neither our analysis nor any other existing theoretical analysis seems to be very successful. For example, our analysis fits well for certain data on acetone–butanol mixtures at 1 bar, but not at 10 bar. The approach of Stefan and Körner [5] led them to two empirical constants: the first allows for that effect of pressure on all mixtures; the second is specific to the mixture considered. By suitable choice of those two constants, an empirical fit can be obtained to a wide range of data, but, as they acknowledge, it would be preferable to substitute a theoretical method.

With that in mind, work is continuing on the effects of bubbles on each other, and the effects of initial conditions (velocity and temperature) in the liquid, in pure fluids and mixtures. It must also be borne in mind that mixtures may alter developed boiling through other phenomena, such as nucleation.

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APPENDIX 1

EVAPORATION OF BINARY LIQUID—SELF-SIMILAR SOLUTION

Consider the region $z > 0$ occupied by a semi-infinite mass of binary liquid at constant pressure and initially having uniform composition and temperature x_∞, T_∞. If T_∞ exceeds the bubble line temperature T_{BL} for that pressure and composition, then the liquid is supersaturated. If evaporation then starts at the plane boundary $z = 0$, then the equations and conditions to be satisfied are:
(Initial conditions: $T = T_\infty$, $x = x_\infty$ throughout)
Equations for diffusion of heat and mass.

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2}, \frac{\partial x}{\partial t} = D \frac{\partial^2 x}{\partial z^2}.$$

Conditions at the evaporating interface, $z = z_i$:

(1) Temperature T_i and composition of liquid x_{li} and vapour x_{vi} to be consistent with the phase diagram (Fig. 1), i.e. the line $T = T_i$ to meet the bubble and condensation line at x_{li}, x_{vi} respectively.

(2) The rate of evaporation to be consistent with
(a) diffusion of heat for latent heat, hence

$$\rho_f h_{fg} \frac{dz_i}{dt} = k \frac{\partial T}{\partial z};$$

(b) diffusion of mass for $(x_{vi} - x_{li})$, hence

$$(x_{vi} - x_{li}) \frac{dz_i}{dt} = D \frac{\partial x}{\partial z}.$$

As shown in [2, 13] these are all met by appropriate error functions for T and x, which lead to constant values of T_i, x_{li}, x_{vi} and a constant value for $z_i/\sqrt{t}$. The solutions are:

$$\frac{T - T_\infty}{T_i - T_\infty} = \frac{\operatorname{erfc}[z/(2\sqrt{\alpha t})]}{\operatorname{erfc}[z_i/(2\sqrt{\alpha t})]}, \quad \frac{x = x_\infty}{x_i - x_\infty} = \frac{\operatorname{erfc}[z/(2\sqrt{Dt})]}{\operatorname{erfc}[z_i/(2\sqrt{Dt})]},$$
$$z_i = K\sqrt{t}.$$

The boundary conditions 1, 2 at the evaporating interface require:

(1) T_i, x_{li}, x_{vi} in equilibrium as indicated above.

$$\text{(2a)} \quad k \frac{(T_i - T_\infty)}{\operatorname{erfc}[K/(2\sqrt{\alpha})]} \frac{\partial}{\partial z} \operatorname{erfc}\left(\frac{z}{2\sqrt{\alpha t}}\right) = h_{fg} \times \frac{1}{2} \frac{K}{\sqrt{t}}.$$

$$\text{(2b)} \quad D \frac{(x_{li} - x_\infty)}{\operatorname{erfc}[K/(2\sqrt{D})]} \frac{\partial}{\partial z}$$
$$\operatorname{erfc}\left(\frac{z}{2\sqrt{Dt}}\right) = (x_{vi} - x_{li}) \times \frac{1}{2} \frac{K}{\sqrt{t}}.$$

The last two equations can be written as

$$\frac{c_p(T_\infty - T_i)}{h_{fg}} = g\left(\frac{K}{2\sqrt{\alpha}}\right),$$
$$\frac{x_{li} - x_\infty}{x_{li} - x_{vi}} = g\left(\frac{K}{2\sqrt{D}}\right),$$

where the function g is defined by

$g(w) = \sqrt{\pi}\, w \exp(w^2) \operatorname{erfc}(w)$, and g^{-1} is its inverse.

The conditions at the interface, T_i, x_{li}, x_{vi}, are determined by the equations involving the function g, and these are normally solved by iteration, using Fig. 1 or the parameters of the mixture which determine Fig. 1. The results of such iterations are shown for some cases in Fig. 3, for the materials used in the current experiments, hexane and octane, at pressure 200 mm Hg, e.g. for the case $x_\infty = 0.8$ and $T_\infty = 90°\text{C}$, iteration arrives at $T_i = 72.9°\text{C}$, $x_{li} = 0.909$, $x_{vi} = 0.606$, since those values give

$$g^{-1}[c_p(T_\infty - T_i)/h_{fg}] = 0.077$$

and

$$g^{-1}[(x_{li} - x_\infty)/(x_{li} - x_{vi})] = 0.267,$$

which are, as required, in the ratio $\sqrt{D/\alpha}$ $(= 1/\sqrt{11.94})$. Hence the systematic plot shown in Fig. 3 was derived, for cases in which $(T_\infty - T_i)$ is constant (20 K) which suggested that the difference between T_i and T_{BL} would be emphasised if experimental conditions were chosen appropriately, towards the left of Fig. 3.

For comparison with other analyses, it is useful to simplify and approximate this analysis, using the following two approximations:

$$g(w) \simeq \sqrt{\pi}\, w, \quad T_i - T_{BL} \simeq (x_{li} - x_\infty)\left(\frac{dT}{dx}\right)_{BL}$$

where $(dT/dx)_{BL}$ is constant, usually evaluated at x_∞.

For acceptable accuracy, these both require $(x_{li} - x_\infty)/(x_{li} - x_{vi})$ to be small (say < 0.2). We than have

$$T_\infty - T_{BL} \simeq T_\infty - T_i + (x_{li} - x_\infty)\left(\frac{dT}{dx}\right)_{BL}$$
$$\simeq T_\infty - T_i + (x_{li} - x_{vi}) \sqrt{\frac{\alpha}{D}} \frac{c_p(T_\infty - T_i)}{h_{fg}} \left(\frac{dT}{dx}\right)_{BL}$$
$$\simeq (T_\infty - T_i)\left[1 + (x_{li} - x_{vi}) \sqrt{\frac{\alpha}{D}} \frac{c_p}{h_{fg}} \left(\frac{dT}{dx}\right)_{BL}\right]. \tag{A.1}$$

This amounts to a reduction in bubble growth by the factor in square brackets. It will be shown in Appendix 2 that this is akin to various other analyses of bubble growth. It will also be shown that the above condition for accuracy is not always met. The linearised analysis thus predicts $(T_\infty - T_i)$ as a constant fraction of $(T_\infty - T_{BL})$. Hence, when it is applied to a very large value of $(T_\infty - T_{BL})$, it can lead to prediction of T_i above the condensation line. That is physically impossible, and is not predicted by the full analysis.

APPENDIX 2

ANALYSES

(a) *Bubble growth in binary mixtures*

In addition to the analysis of hemispherical bubbles by van Ouwerkerk [2] discussed in the text, there have been various analyses of spherically symmetrical, diffusion-controlled bubble growth in binary liquid initially stagnant and of uniform composition and (supersaturated) temperature.

Scriven [1] reached results in the form of computed graphs, and also algebraic approximations for special asymptotic cases such as those with $\rho_g \ll \rho_f$ and $h_{fg} \ll c_p \Delta T$. For such cases in pure liquids his results simplify to $R = 2\sqrt{3/\pi}\, Ja \sqrt{\alpha'}$ For binary mixtures, he defines Ja with $(T_D - T_{BL})$ and appropriate mixture properties and also predicts radius smaller by a factor

$$\left[1 + \sqrt{\frac{\alpha}{D}}(C_{li} - C_{vi})\left(\frac{dT}{dC}\right)_{BL} \frac{c_p}{h_{fg}}\right].$$

This is clearly similar to the approximate result (A.1) above, though not identical, since C is mass fraction.

The analysis of van Stralen [14] can also be seen to be similar. He reaches or adopts the Scriven expression for pure liquids and arrives at a factor for reduction in radius for binary liquids. The factor is

$$1 + \sqrt{\frac{\alpha}{D}\frac{\Delta T}{G}\frac{c_p}{h_{fg}}},$$

where ΔT is the excess of bubble temperature T_B over T_{BL} and G is correspondingly $(x_{lB} - x_{\chi})/(x_{lB} - x_{vB})$. The value of ΔT is not needed provided it is sufficiently small, since the ratio $\Delta T/G$ then reduces to

$$\left(\frac{dT}{dx}\right)_{BL}(x_{lB} - x_{vB}).$$

Hence his prediction is again similar to (A.1) above.

Calus and Leonidopoulos [15] point out the similarity between the above analyses and also show how ΔT in the second analysis can be derived, as $(T_D - T_{BL})F/(1+F)$

where

$$F = (x_{li} - x_{vi})\sqrt{\frac{\alpha}{D}\frac{c_p}{h_{fg}}\left(\frac{dT}{dx}\right)_{BL}}.$$

(b) *Nucleation in binary mixtures*

The approaches considered above, including our own analysis, are "dynamic" or growth analyses, based on consideration of rates of flow of heat and mass. An alternative analysis by Stephan and Körner [5] is a "differential" or nucleation analysis, in which they determine ΔG^+, the difference in Gibbs function for a given equilibrium system due to the change from pure liquid to liquid containing a spherical vapour bubble of volume V''. That ΔG^+ would, of course, be zero in a pure substance if pressures were uniform, since Gibbs function is then the same in vapour and liquid. But pressures are not uniform, due to surface tension, σ. They arrived at a value of ΔG^+ dependent on σ, obtaining, for a pure substance,

$$\Delta G^+ = \frac{16\pi}{3}\sigma^3\frac{V''^2}{(H_{lv}\Delta T/T)^2}.$$

(In dynamic analyses, σ has little or no influence, but here it is essential.) In their corresponding expression for a binary mixture, they found, in effect, that ΔG^+ is reduced because H_{lv} must be replaced by

$$H_{lv} + (x'' - x')\frac{\Delta x'}{\Delta T}T\frac{\partial^2 G}{\partial x^2}$$

(H_{lv} is a transfer enthalpy, i.e. at constant composition). The items H_{lv} and $(x'' - x')$ in this expression also arise in the linearised result of the dynamic analyses (A.1) where $(x'' - x')$ is $(x_{vi} - x_{li})$ and has the effect of reducing bubble growth rate. Here, Stephan and Körner state that it shows the reduction in work of creating a viable bubble, and they conclude that heat transfer to boiling mixtures must be hindered by an amount proportional to $(x'' - x')$.

(c) *Comparison with observation from boiling or bubbles*

Our analysis in the text and the analyses in (a), (b) above all lead to the same conclusion in general terms, and of course bubble nucleation and growth may both be important in boiling. As shown by the experiments reported here, the predictions of growth analysis are supported directly by detailed observation of actual growth of bubbles, at least over the range we covered. To obtain similar support for the predictions of nucleation analyses, it is presumably necessary to observe detailed phenomena of nucleation, such as activation of cavities. Experiments in that field are notoriously difficult, due to sensitivity to minor surface effects, impairing reproducibility. Corresponding support for nucleation analyses has not yet been achieved to our knowledge.

Most authors above have applied their results to the prediction of boiling heat transfer in binary mixtures. For a given heat flux and varying composition, they can be regarded as predicting a temperature difference $T_D - T_{BL}$ which consists of two parts. One part is based on the temperature differences observed for the pure liquids and varies linearly between those values (linearly in molar or mass concentration). The second part allows for the reduction factor discussed in various forms above. It is, in effect, $(T_i - T_{BL})$, the driving potential "lost" to heat diffusion by being used for mass diffusion. The present work on bubble behaviour improves our understanding of that "loss", but as discussed in the text, the boiling situation involves other complications, and no theory yet explains it satisfactorily. Hence results from boiling heat transfer cannot adjudicate between the theories.

The analyses quoted above contain or imply predictions of bubble temperatures and growth rates, which can now be compared with our observations. Those predictions differ from our observations when the approximations used for their analyses and for equation (A.1) are poor. That arises principally when $(x_{li} - x_{\chi})/(x_{li} - x_{vi})$ exceeds 0.2, and also the temperature difference $(T_D - T_i)$ is large. Such cases arise among the tests by Stone [8] particularly with bubbles grown in mixtures containing about 75% octane (over 80 were observed) especially with high supersaturation. The linearised analyses of equation (A.1) or of Scriven or van Stralen then predict bubble growth smaller than we do. Comparing their predictions with our observations would amount to increasing by some 10% the values in the mixture columns of Table 1. However, such a change is within the scatter of the data.

EBULLITION DES MELANGES BINAIRES. ETUDE DES BULLES INDIVIDUELLES

Résumé—On présente des expériences sur des bulles de vapeur individuelles qui croissent sur une paroi plane dans un liquide isotherme initialement stagnant. De tels essais sont bien analysés et compris pour les liquides purs, mais ici les liquides sont des mélanges binaires d'hexane et d'octane en composition variable.

Le résultat principal est que les observations cinématographiques du comportement général de telles bulles (vitesse de croissance, changement de forme, époque et taille à la séparation) ne montrent pas de nouveauté; il y a idendité avec les liquides purs si un changement de paramètre est fait. Ce changement consiste en la substitution de la température correcte d'évaporation de l'interface binaire à la place de la température de saturation du liquide pur. Cette température d'interface est déterminée par référence aux récentes solutions analytiques pour l'évaporation d'un liquide binaire semi-infini par diffusion de chaleur et de masse.

On effectue aussi des observations rapides et détaillées des températures à la paroi sous la bulle et dans la bulle. Elles montrent quelques aspects qui diffèrent nettement des liquides purs (bien que cela n'affecte pas le comportement général). Ces aspects sont expliqués par une analyse détaillée de la diffusion de chaleur et de masse dans une fine couche de liquide (microcouche) sous la goutte.

On considère aussi des implications pour le transfert thermique par ébullition et on montre que cette analyse des gouttes individuelles n'explique pas la réduction du coefficient de transfert entre les liquides purs et binaires. On examine plusieurs explications de cette réduction et on montre qu'il y a une base commune proche de celle déterminée par cette analyse des bulles uniques. Mais une extension à partir de cette base pour prédire les taux de transfert thermique ne convient pas, à moins d'introduire de façon empirique un coefficient dépendant de la pression.

DAS VERDAMPFEN BINÄRER GEMISCHE—UNTERSUCHUNG VON EINZELBLASEN

Zusammenfassung—Es wird über Experimente berichtet, bei denen Einzeldampfblasen an einer ebenen Wand in einer anfangs ruhenden, isothermen Flüssigkeit zum Wachsen gebracht werden. Derartige Untersuchungen sind an reinen Flüssigkeiten schon durchgeführt worden und können zufriedenstellend erklärt und rechnerisch behandelt werden. In der vorliegenden Arbeit werden binäre Hexan-Oktan-Gemische unterschiedlicher Zusammensetzung untersucht.

Als wesentliches Resultat ergibt sich aus Filmaufnahmen, daß das allgemeine Verhalten solcher Blasen (Wachstumsgeschwindigkeit, Gestaltänderung, Abreißzeitpunkt und -größe) keine neuen Probleme aufwirft — es ist identisch mit dem von reinen Flüssigkeiten, sofern ein Parameter geändert wird: anstelle der Sättigungstemperatur für die reine Flüssigkeit ist die tatsächliche Temperatur der binären Verdampfungsgrenzfläche einzusetzen. Diese Grenzflächentemperatur wurde unter Verwendung neuerer analytischer Lösungen für die Verdampfung einer halbunendlichen binären Flüssigkeit bei reiner Wärmeleitung und Diffusion bestimmt.

Weiter wurden eingehend die Temperaturen innerhalb der Blase und der Wand unter der Blase mit hoher zeitlicher Auflösung bestimmt. Es ergaben sich hierbei in mancher Hinsicht deutliche Abweichungen gegenüber reinen Flüssigkeiten (wenngleich ohne Auswirkung auf das allgemeine Verhalten). Diese Abweichungen wurden durch eingehende Behandlung der Wärmeleitung und der Diffusion in einer dünnen Flüssigkeitsschicht unter der wachsenden Blase (Mikroschicht) erklärt.

Weiter werden daraus Folgerungen für den Wärmeübergang bei der Verdampfung gezogen, und es wird gezeigt, daß diese Untersuchung der Einzelblasen von sich aus noch nicht die bekannte Abnahme des Wärmeübergangskoeffizienten binärer gegenüber reinen Flüssigkeiten erklärt. Verschiedene bestehende Erklärungen für diese Abnahme werden untersucht und auf eine gemeinsame Basis zurückgeführt, die derjenigen nahekommt, die wir aufgrund unserer Untersuchungen an Einzelblasen hergeleitet haben. Zur Vorausberechnung der Wärmeübertragung bei der Verdampfung durch einfache Verallgemeinerungen auf dieser Grundlage versagen diese Erklärungen jedoch, es sei denn, ein zusätzlicher druckabhängiger Multiplikationsfaktor wird aus rein empirischen Gründen eingeführt.

КИПЕНИЕ БИНАРНЫХ СМЕСЕЙ — ИССЛЕДОВАНИЕ ОТДЕЛЬНЫХ ПУЗЫРЬКОВ

Аннотация — Экспериментально исследуются отдельные пузырьки пара, растущие на плоской поверхности, расположенной в первоначально неподвижной изотермической жидкости. Такие эксперименты проводились ранее с чистыми жидкостями, и были предложены удовлетворительные обобщенные зависимости. В предлагаемой же работе исследуются бинарные гексано-октановые смеси переменной концентрации.

С помощью киноплёнки зафиксировано поведение пузырьков в таких смесях (скорость роста, изменение формы, время и диаметр отрыва пузырьков) и обнаружено, что оно идентично их поведению в чистых жидкостях. При этом вместо температуры насыщенного пара для чистой жидкости необходимо использовать значение температуры границы раздела для бинарной смеси. Это значение определяется по недавно предложенной аналитической зависимости для процесса испарения из полубесконечного объёма бинарной смеси.

Проведены также детальные измерения значений температур под пузырьками на стенке и внутри пузырьков. Отмечен ряд отличительных особенностей, не свойственных чистым жидкостям (которые, однако, не влияют на общую картину поведения пузырьков). Эти особенности объясняются с помощью детального анализа переноса тепла и массы в тонком слое (микрослое) жидкости под растущим пузырьком.

Рассмотрен также процесс теплообмена при кипении и показано, что сам по себе анализ поведения отдельных пузырьков не позволяет объяснить уменьшение коэффициента теплообмена бинарной жидкости по сравнению с чистой. Рассмотрено несколько возможных объяснений этого уменьшения и показано, что они основаны на общем исходном положении, близком к результатам настоящей работы для отдельных пузырьков. Однако интенсивность теплообмена при кипении может быть рассчитана на этом основании только при введении дополнительного коэффициента, зависящего от давления.