DISCUSSION

Figures 1 and 2 reveal that under oxidizing conditions ($S > 1$), the eventual conversion of NO (i.e., when CO conversion = 1) increases as k increases, as would be expected. The phase plane diagram shown in Figure 3 corresponds to the experimental feed compositions of Tauster and Murrell (1976). The curves are themselves independent of k_1; however, lines of constant catalyst area (a) depend on k_1, and for Figure 3 the value shown in Table 1 is used.

At complete CO conversion, NO conversions of 59.5%, 81.2% and 91% are realized for $k = 1$, 2 and 3, respectively. It is worth noting that Tauster and Murrell (1976) did observe NO conversions in excess of 90% in their experiments.

Schlatter and Taylor (1977), and Tauster and Murrell (1976) had experimentally noted that under oxidizing conditions ($S > 1$), NO conversion (y) becomes independent of catalyst loading as long as CO conversion (x) is close to 1. Hegedus et al. (1979) remarked about this point for $k = 1$, and also that under net reducing conditions ($S < 1$), CO conversion becomes independent of the catalyst area when NO conversion is close to 1. Both these features can also be seen for $k = 2$ and 3 in Figures 1 and 2. Note that this independence occurs at relatively lower catalyst areas when k is larger; i.e., as the catalyst becomes more active in general, as well as more selective for NO.

In conclusion, it is worth remarking that the analysis presented in this work is general, and applies to other competitive reaction systems as well.

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NOTATION

a = active catalyst area
C = species concentration
F = function, defined by Eq. 8
k = catalyst partition factor, $2k_2/k_1$
k_1, k_2 = rate constants
L = reactor length
p_i = constants, defined by Eq. 19
q_i = constants, defined by Eq. 19
$r_\pm$ = constants, defined by Eq. 22
R = constant, $C_{NO,0}/C_{CO,0}$
S = stoichiometry number, $(2C_{O_2,0} + C_{NO,0})/C_{CO,0}$
t = dimensionless reactor length, $ak_1C_{CO,0}(z/v)$
v = fluid velocity
w = dimensionless O_2 concentration, $C_{O_2}/C_{O_2,0}$
$\bar{w}$ = constant, defined by Eq. 22
$w_\pm$ = constants, defined by Eq. 14
x = CO conversion, $1 - (C_{CO}/C_{CO,0})$
y = NO conversion, $1 - (C_{NO}/C_{NO,0})$
z = distance from reactor inlet

Greek Letters

α = constant, defined by Eq. 22
β = constant, defined by Eq. 22
θ = dimensionless reactor length when $S = R$

Subscripts

0 = inlet value

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Bubble Nucleation Studies

Part I: Formation of Bubble Nuclei in Superheated Water by Bursting Bubbles

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The development of a thorough understanding of nucleate boiling requires, among other things, an explanation of the source of the nuclei from which the vapor bubbles grow. Experiments have shown that for boiling in thin liquid films a new mechanism operates to produce bubble nuclei, Mesler & Mailen (1977). The experiment reported here gives further information on this new mechanism when the boiling is not confined to a thin film.

Nucleate boiling is an efficient means to transfer heat that relies on bubbles to augment heat transfer. Bubbles live only a transient existence in nucleate boiling. They grow from tiny nuclei and reach a size that causes them to break, either individually or after joining other bubbles, into the vapor region above the liquid surface. Boiling depends on a source of bubble nuclei for if there are no bubbles there is no boiling. Bubbles start their growth from something very small usually termed a nucleus. In experiments which minimize the presence of nuclei quite high liquid superheats are achieved without ebullition. The usual explanation of a nucleus is that it is a tiny bit of gas or vapor trapped in a crack or pit on the solid surface, Cole (1974). The gas nuclei may come from some gas that remains of that covering the surface before it was wet and the vapor nuclei may come from the remainder of a previously departed bubble which has stayed attached to the solid surface. Nowhere in the literature on nucleate boiling has there been found mention that nuclei might originate in the liquid during boiling because of the complicated motions of interacting vapor and liquid.

The bubbles of nucleate boiling have been studied by numerous investigators at conditions of low heat fluxes and low bubble populations. The advantage of operating under such conditions is that one can observe the behavior of individual bubbles. Indeed, it is from studies under these conditions that much of the present understanding of bubble nucleation during nucleate boiling has been derived. While it is true that studies at low bubble populations simplify matters they are not typical of the usual applications of nucleate boiling which are at higher heat fluxes and much higher bubble populations.

Inspection of the boiling phenomenon shows that bubbles generally form at only a few locations on the surface at low heat fluxes. At higher heat fluxes the bubbles appear at more locations. The usual explanation is that higher surface temperatures allow more sites on the solid surface to function as active nucleation sites. With further increases in the surface temperature and heat flux the physical situation becomes highly disorganized and a clear view of what happens is no longer possible but it has been presumed that an augmentation of the previous conditions occurs even though it cannot be clearly observed. But this presumption may not be entirely correct.

A number of investigators have studied boiling from thin liquid films and some of these have reported measuring lower surface temperatures when boiling from thin liquid films than when boiling from deeper liquid pools, Jakob and Linke (1935), Nishikawa et al. (1967), Mesler (1976), Marto et al. (1977). The possible significance of these reports appears to have been either ignored or neglected. Nevertheless these measurements suggested that some other bubble nucleation source may be operating in nucleate boiling and this source is more effective in thin film boiling. Consequently experiments were done and reported which showed that after a bubble grown from a liquid film burst new bubbles grew from the liquid at the same location, Mesler and Mailen (1977). This occurred repeatedly indicating that in some way bubble nuclei were formed in the process of the bubble bursting. The nuclei that were formed were themselves not seen in photographs but their presence was inferred from the bubbles that grew. Bubble growth indicated also that there was sufficient superheat to permit growth of the nuclei.

A new source of nuclei was shown for thin film nucleate boiling which fortunately provided an opportunity to observe clearly evidence that it occurs. Does the source operate in other than thin films where observations are not so easy? The disorganized state that exists at high heat fluxes and high bubble populations provides many opportunities where bubbles burst through a liquid-vapor interface. Are bubble nuclei produced in all the commotion even though the bubbles do not burst from a film on the surface? An investigation of bubbles bursting from other than thin films would help to access this as a possible source of nuclei. Therefore, an investigation was made of bubbles bursting on the surface of liquid deep enough to provide a view beneath the bubble.

EXPERIMENT

The development of bubble nuclei requires the water in which the nuclei are produced to be superheated. The objective of the experiment was to allow a bubble to burst on the surface of a body of superheated water and look for bubble growth to indicate nucleation.

Several methods were tried to produce a superheated liquid. The arrangement that proved successful was to heat water in a 2.5 cm OD glass tube with a 650 W DVY photographic lamp 18 cm above the interface. A small glass tube with an orifice at the tip was inserted up through a stopper in the bottom of the larger tube. Air supplied to the tube formed a train of bubbles. The water in the test tube was degassed and demineralized. The idea behind this arrangement was to allow an air bubble to burst at the liquid-vapor interface and photograph the bursting and growth of any bubbles that might grow from any nuclei produced. A bonus sometimes accrued to this arrangement because not only were there bubbles that grew but they coalesced to form a large vapor bubble. When the vapor bubble later burst it too caused the subsequent growth of additional bubbles.

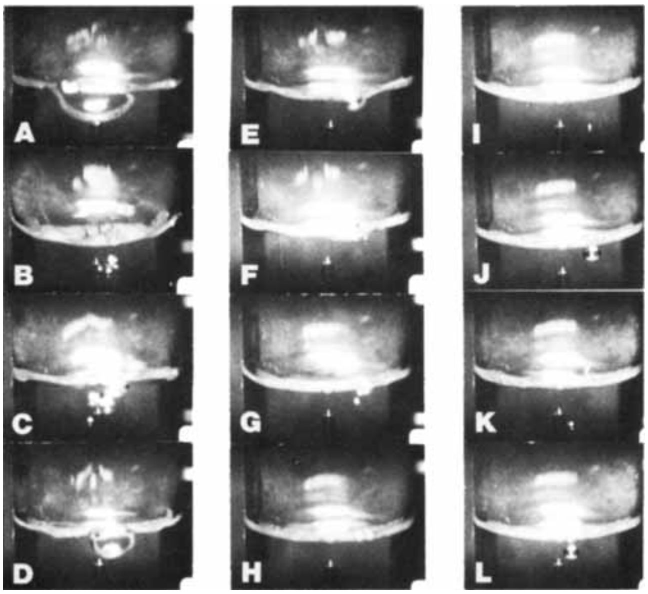

Figure 1. Selected frames from a high-speed motion picture showing new bubbles appearing following the bursting of air and vapor bubbles. The times in ms following the bursting of the air bubble are B-36, C-63, D-103, E-209, F-213, G-264, H-317, I-478, J-505, K-639 and L-665.

High-speed motion pictures at 750 pictures per second were taken of the bursting bubbles. Projection of the film revealed clearly that clusters of new bubbles grew shortly after an air bubble burst at the surface.

Figure 1 shows selected frames which illustrate the bursting of an air bubble and then a vapor bubble. The air bubble is shown in the first frame just before it bursts. The next two frames show the growth of a cluster of bubbles which coalesce to form the large vapor bubble shown in frame D. This vapor bubble is shown somewhat smaller in frame E just before it bursts. The growth of another cluster of bubbles is shown in frame F and G and these have coalesced in frame H. The last four frames show the later growth of two additional bubbles.

The nuclei for the clusters of bubbles are not seen. However, the fact that the cluster of bubbles follows so soon after the bubble bursts indicates that the nuclei for the cluster of bubbles were produced by the bubble bursting. The first bubble in the cluster is visible 6 ms after the first bubble burst but others are not seen until later. A group of four become visible at 30 ms and four more at 50 ms. The bubbles are up to 5 mm beneath the miniscus. By 100 ms the bubbles coalesced to form the large vapor bubble. The vapor bubble shrinks slightly and in another 100 ms bursts. Again a cluster of bubbles is produced. The first of these is seen in only a ms joined by others shortly later. Another is first visible at 36 ms. By 108 ms, these have coalesced.

At 180 ms after the vapor bubble bursts a tiny bubble becomes visible about 5 mm beneath the miniscus. This bubble shown in frames I and J grows slowly taking about 130 ms to surface. At 390 ms after the vapor bubble bursts another tiny bubble becomes visible about 6 mm beneath the miniscus. This bubble shown in frames K and L grows fast enough that it reaches the miniscus in 75 ms. Whether these two bubbles grow from nuclei generated by the bursting of the vapor bubble is not certain but the possibility cannot be ruled out.

CONCLUSIONS

This experiment shows that when an air bubble bursts on the surface of superheated water it produced bubble nuclei. Furthermore, when a vapor bubble bursts it too produces nuclei. Bubbles grown from the nuclei are first seen a few mm beneath the surface. The nuclei often are in clusters. Some bubbles in the clusters appear shortly but others are not seen for several ms. Individual bubbles which grow a few hundred ms later within 6 mm of the surface may also have grown from nuclei from the bursting bubble.

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Part II: Bubble Entrainment by Drop-Formed Vortex Rings

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A bubble bursting on the surface of superheated water causes nucleation of clusters of bubbles a few mm beneath the surface after a few milleseconds, Bergman and Mesler (1981). The cause of the nucleation is not clear but one plausible mechanism is the entrainment of tiny vapor bubbles into the liquid. When a bubble bursts through the interface the liquid film ruptures. Liquid accumulates along the torn edge of the film as the edge rapidly recedes. Drops are formed along the edge of the film and are pulled into the miniscus at appreciable velocities. Do these drops entrain tiny vapor bubbles which become the nuclei for later growth of clusters of bubbles a few mm beneath the surface? This investigation was begun to attempt an answer to this question.

Before addressing the question of entrainment it is first necessary to understand that the impact of a drop onto a surface of the same liquid is a much more complicated phenomenon than might be supposed. A number of studies are found in the literature. These studies fall into two general categories based upon drop velocity. One group of investigators studied the impact of low velocity drops and the other high velocity drops. The drop and surface interactions in each case differ considerably. Curiously, a unified study consisting of both high velocity and low velocity drops was not found.

Two classic studies of low velocity drops falling into a liquid pool are Rogers (1858) and Thomson and Newall (1885). Both studies report that a vortex ring forms when a low velocity drop strikes the liquid surface. Coloring the drop permits the flow of its contents to be seen. This makes the vortex ring visible. The rotation of the vortex ring on its circular axis is directed upwards on the outer periphery, and downwards on the inner. Rogers describes the vortex ring as a coil of colored fluid enfolding a parallel uncolored coil. Bands are visible due to the two fold structure of the vortex ring. The vortex ring formed by a falling low velocity drop appears quite similar to the vortex ring formed by a burst of gas or liquid issuing from an orifice, with a smoke ring being a familiar example. Chapman and Critchlow (1967) photographed the falling drops and report that a spherical drop changing to a prolate spheroid just as it arrives at the surface produces vortex rings with greater penetrating power.

The classic study of high velocity drops was that of Worthington (1908). Using spark photography, Worthington examined drops falling from 40 to 137 cm. Water was the principal fluid investigated but milk was sometimes substituted to illuminate certain aspects of the drop and surface interactions with little change in the properties of the fluids.

Worthington's photographs indicate that the high velocity water drop flattens as it strikes the pool surface. A crater is formed, with the liquid from the drop lining the inside surface of the crater. Jayaratine and Mason (1964) suggest that a thin film of air separates the liquid of the drop from the pool liquid. A film of liquid rises from the periphery of the crater. Milliseconds later, the walls of the crater begin to converge upon the center. Simultaneously, most of the lining of the cavity flows to the bottom of the crater and forms the top of an ascending jet. The jet often pinches off due to surface tension and forms drops. The jet and drops reach a maximum height and then fall back to the pool surface. A series of ripples radiate outward from the point of impact. When a pinched off drop falls back it will often form a vortex ring as was reported by Thomson and Newall. Mitzutani (1977) has published results of a cine-photographic study made at 72 frames/s which shows this for a 3-mm diameter water drop falling 99 cm.

Blanchard and Woodcock (1957) studied entrainment of bubbles by raindrops falling at terminal velocity onto water and report that entrainment depends upon raindrop size. They report small drops about 0.4 mm in diameter produce 2 or 3 bubbles of about 50 μm diameter that are carried only 1-3 mm beneath the surface. The number increases rapidly with drop size as a 2.2 mm diameter drop was observed to produce 50-100 bubbles that were often carried down in a vortex ring to depths of 2-4 cm. The vast majority of these bubbles appeared to be under 50 μm in diameter. On occasions it appeared to them that the vortex ring of bubbles formed not at the moment of impact of the drop with the water but at the collapse of the water column that rises from the bottom of the impact cavity. This, Blanchard and Woodcock observe, is consistent with the photographic study of Worthington and Cole (1897) which shows the water column which was said to form the vortex ring upon collapse. Blanchard and Woodcock remark that Worthington and Cole make no mention of bubbles in the vortex ring but that the bubbles probably passed undetected as only the closest scrutiny will discover them.

There are two subtle puzzling elements in Blanchard and Woodcock's results. One is they attribute the formation of the vortex ring to the collapse of the water column without considering that it could be the return of a pinched off drop that causes the vortex ring. Perhaps this is implied. The other element is the report that only on occasions did it appear that the vortex ring of bubbles was not formed at the moment of impact. Perhaps the "on occasions" simply indicates that they could not be certain of it all the time. A drop of this size impacting at terminal velocity should always form a crater on impact followed by the rising water column. High speed photography which could resolve both these points was not used by Blanchard and Woodcock.

Two other brief references were found which mention bubble entrainment by drops. Rogers (1858) remarks on the tendency for drops to entrain such large bubbles that they spoil the appearance of the vortex ring. Macklin (1976) mentions an un-