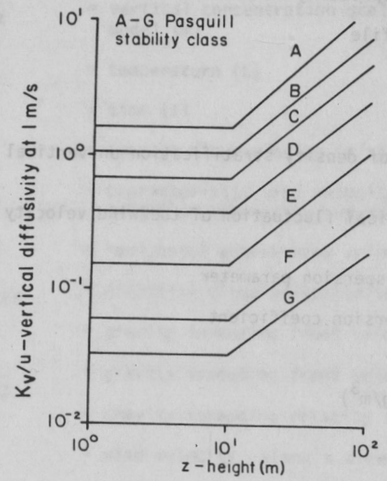

Figure 1. SIGMET vertical diffusivity specification

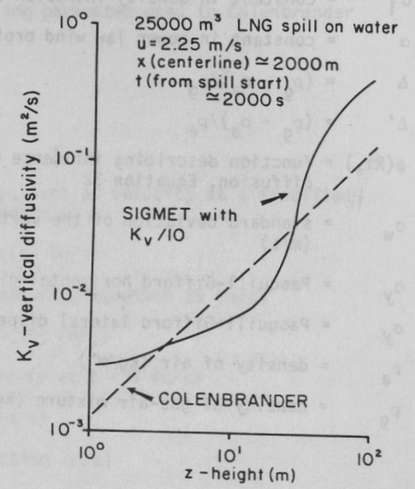

Figure 3. Comparison of SIGMET and COLENBRANDER diffusivity specifications

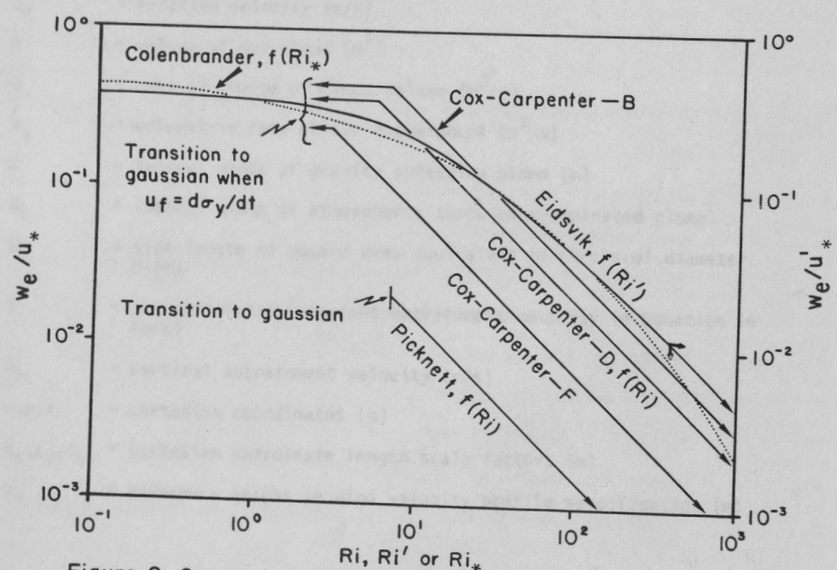

Figure 2. Comparison of entrainment velocity specifications

SUDDEN DISCHARGE OF A SUPERHEATED FLUID TO ATMOSPHERE

B. Fletcher*

Experiments have been carried out on the discharge of superheated fluids (Refrigerants 11 and 114) from an orifice formed in the vapour space of a closed vessel. Measurements have been made both when the vessel top is removed completely and when discharge takes place through vent areas of the order of one per cent of the vessel cross-sectional area.

INTRODUCTION

During the past few years a number of accidents have occurred in which large amounts of flammable or toxic vapours have been released. These releases have taken place from a variety of vessels e. g. process and storage tanks, tank rail-cars, pipelines, and have been caused by any of several mechanisms e. g. venting through pressure relief valves, failure of connecting pipe work and flanges, rupture of vessel during transport etc. [(1), (2), (3)] .

HSE is examining a number of aspects of the hazards presented by such spillages including the behaviour of clouds of dense vapour (4) and methods of dispersion (5).

The situation we are concerned with is that of a vessel containing a superheated fluid (i. e. a fluid stored under pressure at a temperature that would be above its boiling point at atmospheric pressure) which suffers a sudden loss of containment. The objective of the present research is to provide information on the source terms for use in atmospheric dispersion models.

Source models are perhaps the least investigated aspect of dispersion work. The method of release of a fluid into the atmosphere will have an important effect on the physical nature of the release and hence influence the mixing and spread of the ensuing cloud. Releases may be broadly divided into two types: those from above the liquid level i. e. venting of the vapour space, and those from below the liquid level. It is the first of these that attention is directed here. The size of the hole as well as its position plays a significant role; if the hole is small compared with the cross-sectional area of the vessel then the rate of fall of pressure within the vessel will also be small.

*Safety Engineering Laboratory, HSE, Sheffield.

Vapour only will be vented from the hole and the rate of release can be calculated using standard methods. At the other end of the size scale is the catastrophic vessel failure; here the pressure in the vessel drops almost instantaneously. The pressure within the liquid drops below the liquid's saturated vapour pressure and a significant proportion of the liquid flashes to vapour. Liquid can be thrown from the vessel in droplet form by this action and may subsequently evaporate. The likely droplet size will depend among other things on the liquid superheat: at low superheats large droplets can be ejected which fall back either to the ground or into the vessel again; at high superheats the droplets are small and can remain airborne. These finally divided droplets then form an evaporating aerosol whose characteristics change with time.

The sequence of events could also be influenced by the proximity of the initial liquid level to the breach through which venting takes place. When the distance is small and the hole is of an intermediate size, the liquid in the vessel could froth up to the level of the hole. The flow through the breach would then change from one of vapour to a two phase discharge; the flow rate would therefore fall causing the pressure in the vessel to start to rise. This would eventually suppress the boiling causing the liquid level to fall and single phase venting to recommence, and so on. Hence a self-regulating flow system may be established under these conditions such that the liquid/bubble level would just be maintained at the vent level.

EXPERIMENTS

Most of the experiments described below were carried out using a system in which the top of the vessel is removed completely causing a very rapid depressurisation of the vessel; a few discharges have been made through a vent area of the order of one per cent of the vessel cross-sectional area (experiments IV below). The experiments were carried out to try to determine the amount of liquid remaining in a vessel after total rupture in terms of the superheat, liquid depth and vessel size.

Experiments - I A series of experiments were carried out in an aluminium vessel of internal cross section 127 mm x 47 mm and depth 507 mm (See Fig 1); the liquid used was Refrigerant 11 (Formula: CCl_3F, boiling point at 1 atm. : 23·8°C, vapour pressure at 20°C: 189 kN/m²). The top of the vessel could be sealed off by means of a thin acetate diaphragm which could be ruptured as required by a pneumatically operated scalpel blade. The liquid was pumped out of the vessel, through a heater and back into the vessel again to ensure a uniform temperature within the vessel. The temperature in the vessel was monitored by a fast response thermocouple and pressures were measured using piezo-resistive pressure transducers; the signals from these gauges were recorded on a transient recorder and subsequently plotted out on an X-Y recorder. The initial and final depths of liquid were measured on a sight glass.

For each experiment the vessel was partially filled with R-11; the liquid was heated to the required superheat and its level was measured. The diaphragm was burst, and the amount of liquid remaining was measured. Video recordings of the discharge were made.

Figure 2 shows the final depth of liquid (d) divided by the vessel depth (H) plotted against the superheat (ΔT) for different initial liquid levels (d_o). It can be seen from this graph that a) the final depth of liquid relative to the vessel depth does not depend

on the initial liquid level and b) a superheat of about 2°K is required before any loss of liquid occurs. We should qualify a) by saying that for liquid to be ejected the initial liquid level relative to the vessel depth d_o/H must be greater than the value of $\frac{d}{H}$ given by Fig 2. When this level was not exceeded the only liquid lost was that which flashed to vapour on depressurisation and was about 3% for the superheats considered.

Experiments - II A few experiments similar to those described above were carried out using Refrigerant 114. (Formula: $CClF_2$ $CClF_2$, boiling point at atm. : 3·6C, vapour pressure at 20°C : 274 kN/M·²).

Figure 3 shows the results obtained together with those for experiments in a cast iron tube of cross-section 100 x 100 mm. Comparing Figs 2 and 3 it can be seen that the amount of liquid remaining in the vessel is less in the case of R-114.

Experiments - III A number of transparent vessels were constructed so that the processes inside them could be observed. They consisted of lengths of pyrex tubing joined together by metal bands which were used to house the instrumentation. R-11 was used for these experiments. Immediately after depressurisation a vapour cloud formed above the liquid; this was subsequently displaced from the tube. Heterogeneous boiling took place from nucleation sites at solid/liquid interfaces. At low superheats, nucleation took place only from the instrumentation band; at higher superheats, nucleation started from both the vessel base and the band. Bubbles from these sites rose through the liquid expanding rapidly and forming sites for further nucleation. When the initial liquid level and the degree of superheat were sufficiently high, droplets of liquid were ejected from the tube. Collection of these droplets confirmed, that almost all of the loss from the vessel was in liquid form; only a few per cent flashed to vapour.

Observation of the nucleation process within the vessel showed that, when boiling took place at the ring only, the liquid below this level seemed to take no part in the subsequent sequence of events: nucleation never moved down below the level of the ring.

In order to determine the role of the position of the nucleation site in relation to fluid depth, experiments were carried out with the instrumentation ring at three different heights. In a pyrex vessel of internal diameter 95 mm and height approximately 1.7 m, the distances from the base were zero (instrumentation in the vessel base), 115 mm and 210 mm; three different depths of liquid were used for each position. The height h to which the liquid rose up the tube above the initial liquid level on depressurisation was measured from video recordings with superheats up to approximately 7°K. Figure 4 shows an example of the results for the instrumentation ring at 210 mm; d'_o is the depth of the liquid measured from the ring i. e. from the nucleation site. This shows that for a fixed position of the nucleation site the important liquid height is that above the nucleation position, ie the boil-up height should be non-dimensionalised with respect to this parameter. Figure 5 shows that the amount of liquid below the nucleation position does not have a significant effect on the height to which the liquid boils up relative to the height of liquid above the nucleation position.

Experiments - IV Experiments were also carried out in the pyrex vessel with the instrumentation in the base with venting restricted to a small circular orifice approximately 1 per cent or $\frac{1}{4}$ per cent of the vessel cross sectional area. In each experiment the initial liquid depth was about 210 mm. Figure 6 shows the effect of these restrictions on the height risen by the liquid; it can be seen that the height is greatly reduced when discharge takes place through a small orifice.

A special situation has been found to arise when similar experiments are carried out using a long (order of 1 m) column of liquid. It was found possible to depressurise the tube without the liquid boiling. A metastable state was thus obtained: following some perturbation, a small bubble began to rise up the tube growing very rapidly until it occupied virtually the whole of the tube cross-section. This large bubble pushed a slug of liquid ahead of it up the tube gradually catching up the liquid surface. This mechanism could lead to a jet of liquid being ejected from the orifice.

DISCUSSION OF RESULTS

The physical situation we have been considering is one of a liquid, stored at a low degree of superheat under its own vapour pressure, suddenly being depressurised to atmospheric pressure. For a bubble to remain in equilibrium the pressure inside the bubble must exceed that in the liquid by an amount equal to the force due to surface tension which tends to collapse the bubble. The internal pressure of the bubble corresponds to the saturated vapour pressure at the liquid temperature and hence the liquid must be superheated for nucleation to take place. This should explain why in Fig 2 the value of ΔT does not tend to zero as $\frac{d}{H}$ tends to one. If we consider the degree of superheat ΔT required for vapour nucleation it can be shown that

$$\Delta T \simeq \frac{4 R T_{SAT}^2 \sigma}{L M \delta P_L} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

if $\rho_L >> \rho_V$ and $\frac{4\sigma}{P_L \delta} \ll 1$ where T_{SAT} is the saturation temperature of the liquid at pressure P_L. ρ_L and ρ_V are the liquid and vapour densities respectively, σ is the surface tension, L is the latent heat of vapourisation, R is the universal gas constant, M is the molecular weight and δ is the diameter of the vapour nucleus. If ΔT_{ONB} (superheat for the onset of nucleate boiling) is the value of ΔT for which $\frac{d}{H} = 1$, then from Fig. 2 we could take a value of ΔT_{ONB} for R-11 of about 1.9°K. Using this value in the above equation with the appropriate physical values of R-11 we can derive a value of δ. With this we could work out ΔT_{ONB} for any other liquid in the same vessel (e.g. ΔT_{ONB} for R-114 would be 1.1°K). In this way we can non-dimensionalise the results shown in Figs 2 and 3. Figure 7 shows each set of data expressed in this way: all the points now lie reasonably well on one curve.

It may be possible, using Fig 6, to get a rough estimate of the amount of a fluid which remains in a vessel after its rupture which is a matter of some uncertainty (see for example ref (1)).

Assuming that following the catastrophic failure of a vessel a homogeneous

mixture of liquid and vapour is produced, the density of this mixture would be

$$\left\{ \frac{m_V}{M_O} \cdot \frac{1}{\rho_V} + \left(1 - \frac{m_V}{M_O}\right) \frac{1}{\rho_L} \right\}^{-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where m_V and M_O are the mass of vapour produced and the initial mass of liquid respectively.

If the tank was originally full, the mass of liquid, m, remaining in the tank after depressurisation is given by

$$\frac{m}{M_O} = \left\{ \frac{m_V}{M_O} \frac{\rho_L}{\rho_V} + \left(1 - \frac{m_V}{M_O}\right) \right\}^{-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

However, if venting takes place through a small orifice, the liquid would only boil-up to a fraction k of its height for catastrophic failure (k being found from Fig 6).

If we call the mass remaining in this case m' we have

$$\frac{m'}{M_O} = \frac{1}{k} \left\{ \frac{m_V}{M_O} \frac{\rho_L}{\rho_V} + \left(1 - \frac{m_V}{M_O}\right) \right\}^{-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$\frac{m_V}{M_O}$ is the theoretical flash which can be evaluated for a liquid from its physical properties and its initial conditions.

Assumptions have been made in deriving equations (2) to (4) and these should be borne in mind. Table 1 lists incidents involving rail cars from which superheated liquids were lost through relatively small punctures and compares the percentage of the mass of liquid reported to have been left in the car after the rupture with the values calculated from equation (4). The values are surprisingly close.

TABLE 1 - Comparison of the Actual and Calculated Amounts of Liquid remaining in punctured Rail Cars.

Incident	Liquid	Percentage of Mass remaining	
		Reported	Calculated
Pensacola (6)	Ammonia	50	40
Mississauga (2)	Chlorine	10	13
Youngstown (7)	Chlorine	44	37

SYMBOLS USED

d	=	final depth of liquid (m)
d_o	=	initial depth of liquid (m)
d_o'	=	initial depth of liquid measured from nucleation site (m)
h	=	boil-up height (m)
H	=	vessel depth (m)
k	=	boil-up height fraction with a small orifice
L	=	latent heat of vapourisation (J/kg)
m	=	mass of liquid remaining after catastrophic failure (kg)
m'	=	mass of liquid remaining after venting through a small orifice(kg)
m_v	=	mass of liquid flashing to vapour (kg)
M	=	molecular weight (kg/k mol)
M_o	=	initial mass of liquid (kg)
P_L	=	pressure in liquid (N/m^2)
R	=	universal gas constant (J/kmol ^oK)
T_{SAT}	=	saturation temperature (^oK)
ΔT	=	superheat (^oK)
ΔT_{ONB}	=	superheat for the onset of nucleate boiling (^oK)
δ	=	diameter of vapour nucleus (m)
σ	=	surface tension (N/m)
ρ_L	=	liquid density (kg/m)
ρ_v	=	vapour density (kg/m)

Acknowledgement - The author would like to thank Mr. A. E. Johnson for assistance in carrying out the experiments. The paper is contributed by permission of the Director of Research and Laboratory Services division, Health and Safety Executive.

REFERENCES

1. Dept Employment, 1975, "The Flixborough Disaster; report of the court of inquiry" HMSO, London.

2. "Report of the Mississauga railway accident inquiry" 1980, Canadian Government Publishing Centre, Supply and Services Canada, Catalogue No T22-50/1981E.

3. Slater, D.H., 1978, Chem & Ind, 295

4. McQuaid, J., 1980 "Field Trials on the Release of Heavy Gases", Proc. 10th International Technical Meeting on Air Pollution Modelling and its Applications, Oct. 23-26 1979, Rome, ed C. Morawa.

5. Moodie, K. 1981, "Experimental Assessment of a Full Scale Water Spray Barrier for Dispersing Dense Gases", I.Chem.E. Symposium "The Containment and Dispersion of Gases by Water Sprays", Nov. 11, 1981 Manchester.

6. NTSB, 1978, "Railroad Accident Report: Louisville and Nashville Railroad Company Freight Train derailment and puncture of anhydrous ammonia tank cars at Pensacola, Florida, November 9 1977" National Transportation Safety Board, Washington DC, Report No NTSB-RAR-78-4

7. NTSB, 1978, "Railway Accident Report: Derailment of Atlanta and Saint Andrews Bay Railway Company freight train, Youngstown, Florida, February 26 1978" National Transportation Safety Board, Washington DC, Report No NTSB-RAR-78-7.

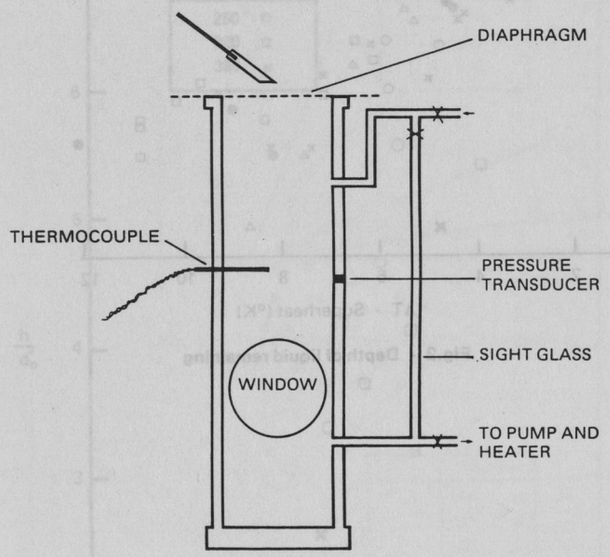

Fig. 1 - Aluminium vessel

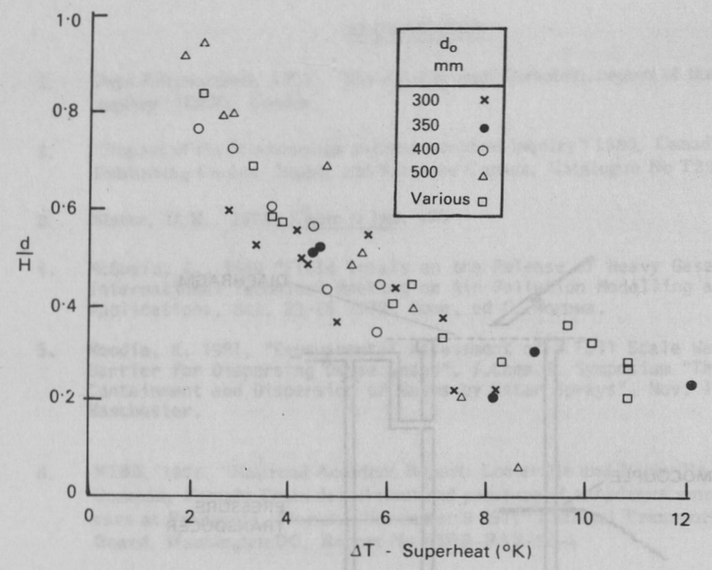

Fig.2 - Depth of liquid remaining

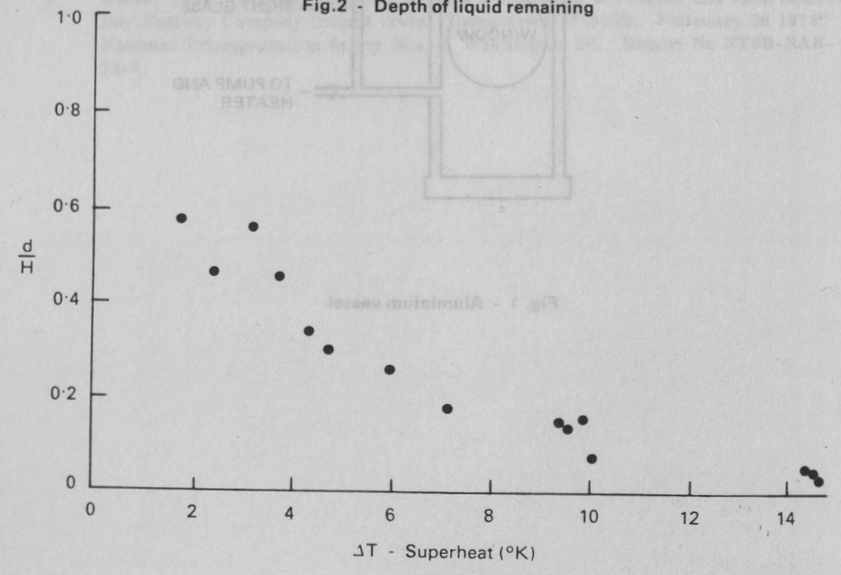

Fig.3 - R - 114 results

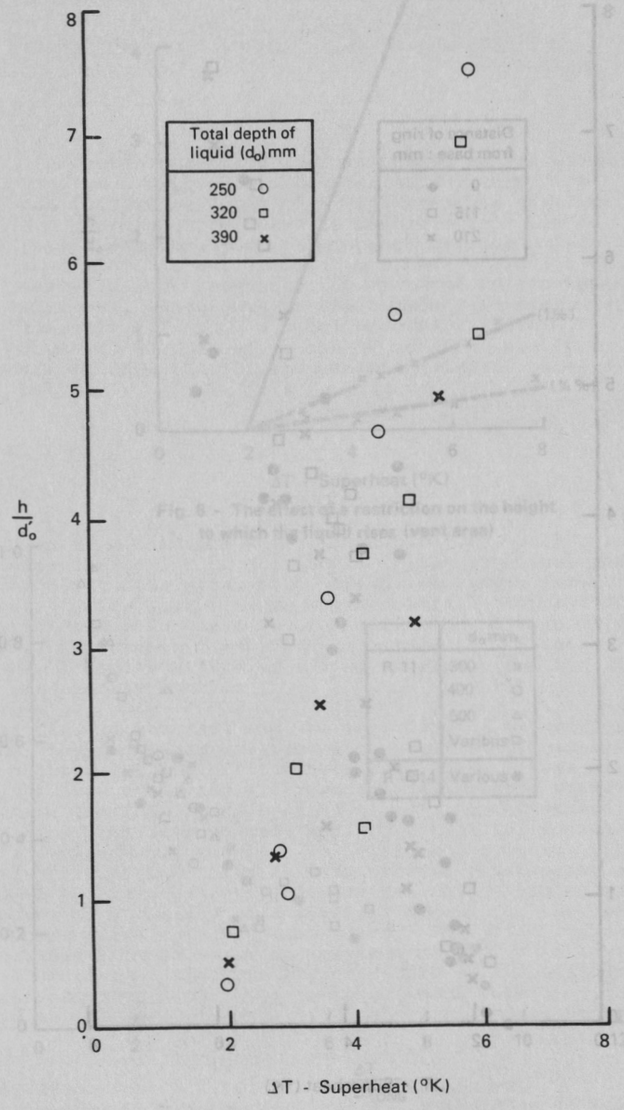

Fig. 4 - Boil-up height for nucleation 210 mm above the base

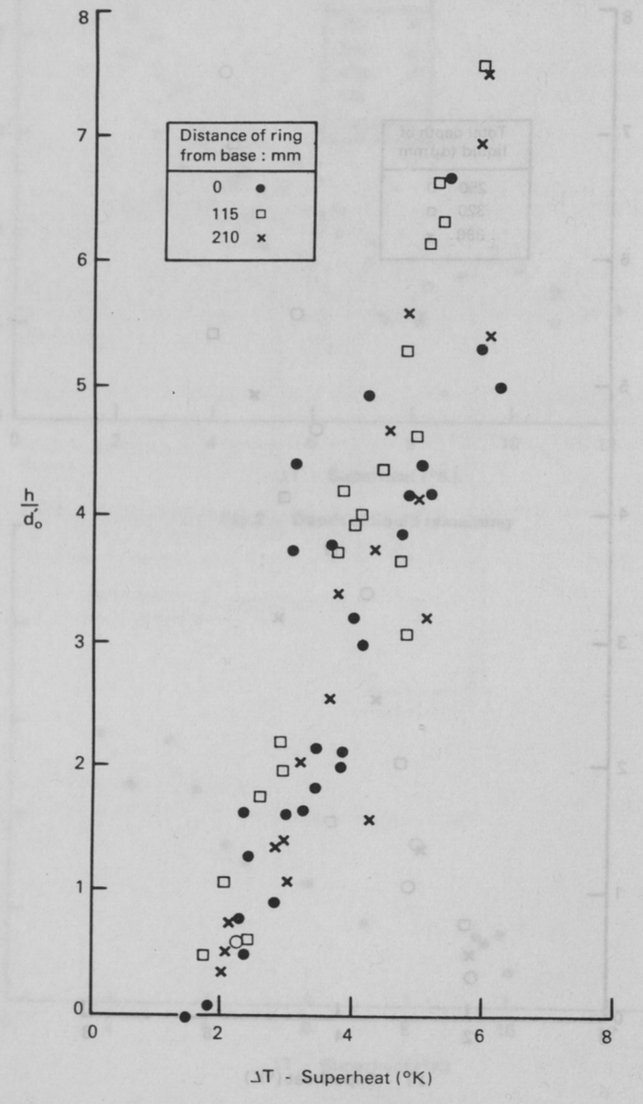

Fig. 5 - Effect of nucleation position on boil-up height

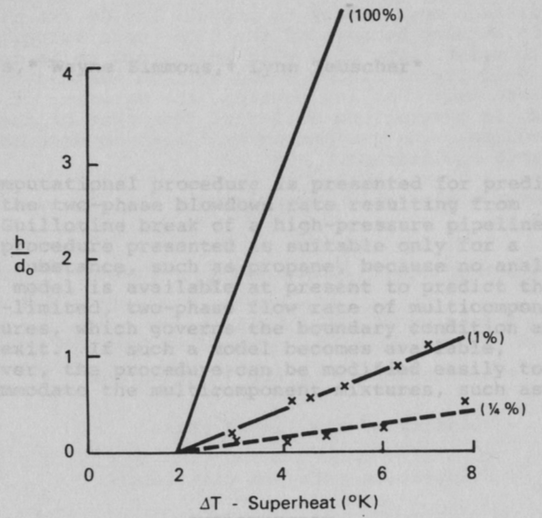

Fig. 6 - The effect of a restriction on the height to which the liquid rises (vent area)

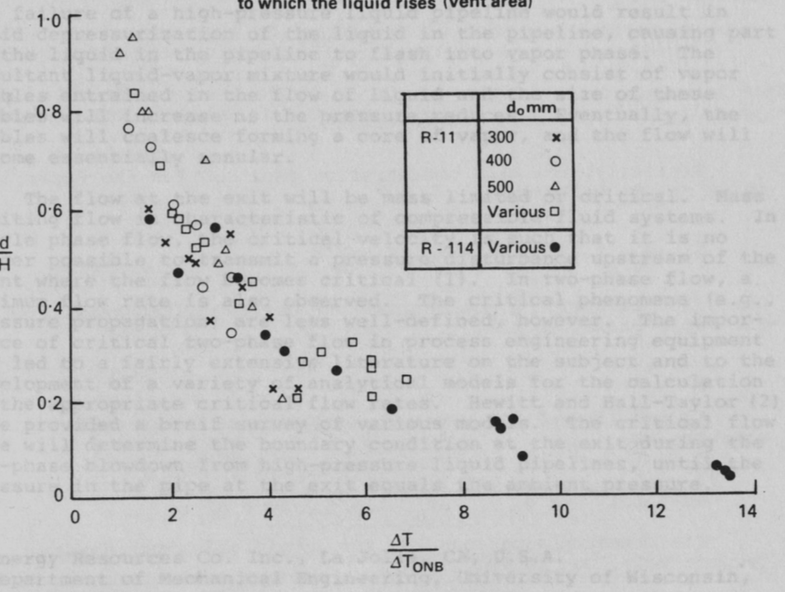

Fig. 7 - Depth of liquid remaining