SRD R 152

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SAFETY AND
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DENZ – A COMPUTER PROGRAM FOR THE CALCULATION OF THE DISPERSION OF DENSE TOXIC OR EXPLOSIVE GASES IN THE ATMOSPHERE

L. S. Fryer and G. D. Kaiser

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July 1979

UNITED KINGDOM ATOMIC ENERGY AUTHORITY
Wigshaw Lane, Culcheth Warrington
WA3 4NE

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DENZ – A computer program for the calculation of the dispersion of dense toxic or explosive gases in the atmosphere

by

L. S. Fryer and G. D. Kaiser

SUMMARY

The report consists of two parts. The first is an introduction to the atmospheric dispersion of vapours that are denser-than-air, together with reasons why this subject is of interest. The remainder of the report consists of the development of a model with which calculations of the consequences of 'puff' releases of chemically toxic or flammable gases may be made and gives a description of a computer code, DENZ, in which the model has been programmed.

Some of the work reported in this paper was performed in connection with a contract for the Health and Safety Executive. The views expressed are those of the authors and do not necessarily reflect the views or the policy of the Health and Safety Executive.

July 1979

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1. INTRODUCTION

The purpose of this report is to describe a recently written computer code, DENZ, which is intended for the study of the consequences of accidentally releasing large quantities of 'heavy' – that is, denser-than-air – chemically toxic or flammable gases to the atmosphere. It also contains a discussion of the reasons why the study of such materials is necessary and describes the characteristic features of their behaviour. The first three sections can be regarded as an introduction for those unfamiliar with the topic.

1.1 Reasons for studying dense gases

There is an ever increasing interest and concern among the public about the risks incurred by the activities associated with the manufacture, storage and transport of potentially hazardous chemicals. This concern has been fueled by a number of incidents that have taken place during the past few years. For example, in the UK, there was a devastating explosion at the Nypro plant at Flixborough[1] in 1974. Recently, a lorry carrying propylene crashed into a camp site in Spain[2] releasing a cloud of vapour which, on being ignited, killed over a hundred and fifty people. In November 1977 40 tonnes (Te) of anhydrous ammonia was accidentally released from a pressurised tank car after a train derailment at Pensacola, Florida,[3] killing two people and injuring forty six.

In these, and other, incidents, the risk to the public arose because there was an accidental release of toxic or flammable gases to the atmosphere. It is often the case that the most likely way in which the public can be harmed during the manufacture, storage and transport of chemicals is by the accidental escape of such materials and the recent study of the complex of industrial installations at Canvey Island[4] confirms this observation. The understanding of the atmospheric dispersion of toxic and explosive vapours is, therefore, an essential element in the study of the safety of chemical plant. One of the most important properties of such vapours is that many of them are denser-than-air and, as is shown in the following, there are some surprising examples of denser-than-air behaviour for gases that, at first sight, should be buoyant.

To begin with, there is a host of gases that are dense because their molecular weight exceeds that of air. Chlorine is an example of a dense toxic vapour, while the petrochemical industry produces and transports a range of flammable dense hydrocarbons such as propane, butane, and propylene. Next, methane (or natural gas consisting largely of methane) is a gas which has a molecular weight smaller than that of air, but which is dense if released at its boiling point of −161°C. Natural gas is often stored or transported as a liquid and a cold, dense vapour can be generated if LNG should be spilled onto land or water.

A superficially surprising example of a gas that can at times form part of a denser-than-air mixture is ammonia, which is chemically toxic. This has a molecular weight of only seventeen and, at its boiling point of −33°C, the pure vapour is less-dense-than-air at 20°C. Nonetheless, there are several examples of accidental releases of ammonia from pressurised containers in which the resulting gas cloud was denser-than-air,[3,5-9,31] or at least non-buoyant. The reason for this is as follows. If ammonia is kept as a liquid at ambient temperature, it is under considerable pressure. If the vessel containing the ammonia should fail – as happened in the USA in May 1976 when a road tanker drove off an elevated section of freeway near Houston and burst on falling to the ground[5] – there is immediate bulk boiling of the liquid. The heat made available by cooling the ammonia to its boiling point is usually sufficient to vapourise about twenty percent of its mass. The vigour of the bulk boiling process is such that most, if not all, of the remaining liquid may be thrown into the air as a fine aerosol. At the same time, air is entrained and supplies heat with which to evaporate the ammonia droplets so that a mixture of air and ammonia, possibly at the boiling point of ammonia, is formed. This can be denser than the surrounding air.[10] This is not to say that such a mixture is always denser-than-air. It is only if the circumstances favour the release of a substantial percentage of the ammonia as fine liquid droplets, that the formation of a dense vapour is to be expected.

Finally, hydrogen fluoride, a toxic gas used by the nuclear industry during the fuel manufacturing process and by the chemical industry as a catalyst in alkylation plants, is an interesting curiosity. Its molecular weight is nominally twenty but, as a pure vapour, it is highly associated and consists of a mixture of hexamer and monomer with an effective molecular weight of about seventy. Disassociation takes place as the hydrogen fluoride is diluted with air, but the heat required to do this is extracted from the mixture and tends to keep it denser than the surrounding air. It is fair to point out, however, that in contrast to the case of the ammonia described above, there is no known example of a large scale accidental release in which this density effect has been observed.

From the foregoing list of examples – which is far from complete – it is apparent that a knowledge of the way in which 'heavy' toxic and flammable vapours disperse in the atmosphere is an essential part of any analysis of the risk incurred as the result of the activities of the chemical industry.

1.2 Plan of the report

Section 2 contains a qualitative discussion of the characteristic features of the atmospheric dispersion of 'heavy' vapours. The concept of gravitational slumping is introduced and illustrated by referring to experiments and to accounts of actual accidental releases. The suppression of the entrainment of air in the presence of a density gradient** is also discussed.

Section 3 is devoted to a discussion of the influence of the source on the subsequent atmospheric dispersion. It is always necessary to ask a number of questions. Is the material kept as a refrigerated liquid, or pressurised at ambient temperature? What is the size and position of the hole through which it emerges? Does the emerging jet impinge onto a surface? Does refrigerated liquid fall onto land or water? Is the emerging jet single-phase or two-phase? These questions reveal that there is a considerable variety of potential source terms. Section 3 explains how these can have greatly differing effects on the subsequent atmospheric dispersion and discusses the uncertainties that exist and, at present, make it impossible to model the release of 'heavy' vapours in all conceivable circumstances.

Section 4 contains a description of a mathematical model for the 'puff' release of dense gases. This model incorporates gravitational slumping, the heating of the cloud by the ground and a prescription for the entrainment of air in the presence of a density gradient. The way in which the model may be used to calculate hazard ranges for toxic and explosive gases is described, and its use as the basis for consequence calculations whence f-N lines* can be generated for toxic gases outlined. Finally, the validity of the model is discussed. Section 5 describes the calculations actually carried out by DENZ and Section 6 describes the necessary control cards and input. Appendix 1 contains a flow chart for DENZ. Appendix 2 consists of a brief description of necessary details of computer language, store required and so on. Appendix 3 contains a summary of notation. Appendix 4 consists of a list of sub-programs and a brief description of their purpose. Examples of the type of input required are given in Appendix 5.

2. CHARACTERISTIC FEATURES OF THE ATMOSPHERIC DISPERSION OF 'HEAVY' VAPOURS

The most interesting characteristic of the dispersion of these gases is the phenomenon of gravity driven slumping, which may best be illustrated by reference to experiments and actual incidents.

Recently, the Dutch Ministry of Social Affairs has sponsored an experiment in which 1 Te of refrigerated Freon-12 was poured onto water.[12,13] The subsequent vigorous boiling process lasted for about five seconds during which a mixture of Freon and air was formed in the approximate shape of a cylinder some 5-6 metres in height and 12 metres in radius, as shown in Fig. 1a. This implies that the vigour of the boiling was such that the Freon entrained some ten times its own volume of air and that the average density of this initial cylinder was 1·25 times that of the adjacent atmosphere. Immediately, the 'puff' began to slump in all directions, (see Fig. 1b) until eventually its height decreased to a small fraction of a metre, as shown in Fig. 1c.

The United Kingdom's Health and Safety Executive has also sponsored a series of experiments in which quantities of Refrigerant-12, pre-mixed with air, were released to the atmosphere as 'puffs'.[14] The releases took place from a 'tent' which is basically a box with concertina-like sides (see Fig. 2), into which about 100 kg of Refrigerant-12 can be pumped. The sides of the tent were allowed to collapse by remote control and Figs 3a and 3b, which are photographs of an experiment which took place when

* *An f-N line for a toxic gas is a plot of the frequency, f, with which a release may occur and put N or more people at risk, where the risk can be that of death or illness or any other consequence chosen by the user.*

** *Wherever the words 'density gradient' appear in this report, a stabilising density gradient is implied.*

there was no wind, well illustrate the phenomenon of slumping. Wind tunnel experiments carried out at the Warren Spring Laboratory, using the gas BCF, also demonstrate slumping.[11]

As far as accidental releases are concerned, it is notoriously difficult to extract useful information from eye-witness accounts; however, on February 1, 1961 there was a train derailment in Louisiana which caused the puncture of a tank car and allowed 30 Te of chlorine to escape. This incident is reported in Reference 51 which includes a map indicating the 'approximate maximum limits' of the chlorine cloud. These limits are about a quarter of a mile upwind and a quarter of a mile to each side of the source. Three miles downwind the cloud was about three miles across. These numbers are indicative of the broad clouds caused by gravitational slumping. There are records of several other accidental chlorine releases, descriptions of which have been obtained from the Chlorine Institute,[52] but there are no eye-witness accounts of the way in which the escaping gas spread. Ironically, perhaps, it is ammonia that provides the best-documented evidence for the occurrence of gravitational slumping in large scale releases of dense vapours.

The recent crash at Houston of a road tanker carrying 19 Te of anhydrous ammonia under pressure[5] has already been mentioned and Fig. 4 is a photograph taken about one minute after the accident from a building north of the release point. The wind direction is from right to left on the photograph and the 'tongue' of vapour shown travelling towards the left of the picture can readily be explained if the mixture is denser-than-air. Figure 5, taken from a helicopter a few days later, shows the area of grass burnt by the ammonia, and demonstrates that the vapour slumped in all directions. The sharp edges seen in some directions are characteristic of 'heavy' vapour clouds.

Another accidental escape of anhydrous ammonia occurred at Potchefstroom, South Africa in 1976[6] when a pressurised vessel failed spontaneously and some 30 Te of ammonia was released. Eye witness accounts speak of an 'immediately resulting' visible cloud some 150 m in diameter and 20 m in height. If all of the ammonia was contained in this 'puff', the mass of air 'immediately' entrained was about ten times that of the ammonia. The cloud remained at ground level, drifted slowly towards a nearby town and increased in width to about 350 m.

A remarkable example of a release of ammonia from a pressurised container took place at Pensacola[3] in November 1977. Some 40 Te escaped rapidly from a tank car and was picked up on the radar at the nearby airport, which was directly upwind. After about five minutes, the vapour cloud was observed to be 'about a mile across'.

The above examples serve to illustrate that the phenomenon of gravitational slumping is a powerful one that can lead to the rapid formation of broad clouds which may affect people standing to one side or even upwind. Figure 5, for example, shows that the visible cloud from about 20 Te of ammonia, suddenly released from pressurised containment, can become several hundred metres in breadth. In Section 4.2 it is shown that this slumping can readily be explained by a liquid column analogy.

The second characteristic feature of dense gas dispersion is that, once slumping has terminated, the action of atmospheric turbulence dilutes the cloud in such a way that the rate of growth of the cloud height is considerably smaller than that expected for a passive plume. That is, the entrainment of air is suppressed in the presence of a density gradient. This phenomenon is illustrated by the releases carried out at Porton.[14] In Section 4.4 this effect is modelled using entrainment criteria derived from water tunnel experiments in which liquids of differing density were allowed to flow relative to each other.

As the entrainment of air proceeds, the 'heavy' vapour is heated by turbulent natural convection and by forced convection, if it is cooler than its surroundings. It may also be directly heated by the rays of the sun and there may be chemical reactions within the cloud (for example, ammonia dissolved in droplets reacting with atmospheric CO_2) which liberate heat. The evaporation or condensation of droplets may also provide sources or sinks of heat. In principle, all of these ways of heating or cooling the plume should be taken into account. The model developed in this report, however, concentrates on turbulent natural convection.

As the cloud is diluted and becomes warmer, its density approaches that of the surrounding air. It becomes increasingly like a passive gas, and, in due course, may be treated as a 'conventional' plume using standard models of atmospheric dispersion.[15]

A mathematical model of the atmospheric dispersion of cold, 'heavy' vapours is given in Section 4; this incorporates the features described in the foregoing. Before it is possible to describe this model, however, it is necessary to add one further characteristic feature of dense gas dispersion, which is that the nature of the source has a profound effect on the subsequent behaviour of the 'puff' or plume. Two possible sources have already been mentioned. In one, the boiling of Freon-12 on water caused the vigorous entrainment of about ten times its volume of air and the formation of a cylinder.[12] In another, the catastrophic failure of a vessel containing anhydrous ammonia under pressure also caused the entrainment of about ten parts by volume of air, and the formation of a 'heavy' cylinder.[6] In surveying the whole range of ways in which chemically toxic or explosive materials are manufactured, stored and transported it becomes clear that there is a large number of possible sources. These may occur because of the spillage of refrigerated liquid onto land, or onto water; or from a variety of ways in which a pressurised container might fail, or for other reasons. A brief survey of some of the possible modes of release is given in the following section.

3. SOURCE TERM FOR THE ATMOSPHERIC DISPERSION MODEL

As has been discussed in the foregoing, one of the most difficult problems encountered when studying the release of chemically toxic or flammable vapours is to determine what effect, if any, the way in which the material escapes has on the subsequent atmospheric dispersion. This is best illustrated by considering some examples.

Suppose that there is a tank containing pressurised liquefied gas at ambient temperature (see Fig. 6) and that this tank is pierced by a missile, or a valve is accidentally sheared off, or a connecting pipe fractured, or a hole appears because of the spontaneous failure of the tank.

3.1 Pressurised tank – small hole in vapour space

If the orifice through which the vapour emerges is in the vapour space (V in Fig. 6A) and has an area a' which is small compared with that of the liquid surface, A_S, pure vapour is emitted at a rate which can be calculated making use of the pressure inside the tank, the area of the hole and a knowledge of the thermodynamic properties of the gas in question.[16,17] It will emerge as a jet of vapour alone into which air is entrained and its dilution and subsequent dispersion can be estimated by methods such as those described by Ooms.[18] Because the hole is, by definition, small, the rate of release is small compared to that which can be envisaged for some of the other release mechanisms to be discussed in this section.

3.2 Pressurised tank – large hole in vapour space (catastrophic failure)

If the area a' is large, that is, a significant fraction of A_S, a different picture emerges, see Fig. 6B. The pressure is relieved suddenly and bulk boiling of the liquid occurs. The fraction of the liquid that boils can be calculated from simple considerations of heat balance.[19] The vigour of the bulk boiling process is such that much if not all of the remaining liquid, now at its boiling point, can be expected to be thrown into the air in finely fragmented form.[20,21] At the same time, considerable turbulence is generated and air is entrained. This air is cooled while evaporating the liquid droplets, which can be shown to be so small that most if not all of them fall out of the vapour cloud over a time scale that is long compared with that required for their evaporation.[10] This particular mechanism of release, therefore, has a significant influence on the input to a subsequent atmospheric dispersion calculation. It affects the total amount of material thrown into the air, making the difference between just the vapour fraction (which is 10-20% for a range of pressurised gases) and the total contents of the tank. It causes the rapid entrainment of considerable quantities of air so that there is an initial and presumably advantageous dilution which, as has already been seen, can be about a factor of ten by volume. The entrained air is cooled by evaporation of the liquid droplets and this affects the density of the cloud. Indeed, for the particular case of ammonia this effect can make the difference between the ammonia being buoyant or denser-than-air. Finally, depending on how much air has been entrained and on the latent heat of the liquid, there may be a fine aerosol of suspended liquid droplets contained in the cloud.

3.3 Pressurised tank – hole of intermediate size in vapour space (Fig. 6C)

The phenomena described in the foregoing have been verified by experiments with anhydrous ammonia described in Reference 20 and by experiments with propylene described in Reference 21. The experiments in Reference 20 have also been filmed and show that a slow rate of escape through a pipe leading from the top of a small dewar flask of ammonia container causes little or no liquid droplet entrainment. When the lid of the flask is suddenly released, however, the whole contents become airborne and there is no evidence that any of the ammonia falls to the ground.

Between these two extremes there must be some critical value of a'/A_s below which there is essentially no liquid droplet entrainment and another, higher, critical value above which there is complete entrainment. Between these figures the airborne liquid fraction f_a should be some function of a'/A_s; the function should also contain some dependence on the temperature and the latent and specific heats of the material in question. To the authors' knowledge, however, the experiments with which it should be possible to determine f_a have not been done, although some experiments have been carried out in which water at high temperature (> 100°C) and pressure was allowed to escape from a container through a pipe the diameter of which could be changed from experiment to experiment.[22] Figure 7* shows a typical set of results giving the fraction of the original mass of water remaining in the vessel as a function of diameter $d = 2\sqrt{a'/\pi}$. It is apparent that, for water under these conditions, a'/A_s > 0·01 defines a 'large' hole since a considerable percentage of water escapes to the atmosphere as liquid droplets through such a hole.

Meanwhile, a general scheme of calculation with which it is possible accurately to calculate the rate and composition of a release through a hole of arbitrary shape, size and position from a vessel containing a gas liquefied under pressure does not exist†. Since the airborne liquid fraction must in turn have an important effect on the density of the source term for the atmospheric dispersion model – with ammonia, for example, it can make the difference between a buoyant mixture and a denser-than-air mixture – it is concluded that the atmospheric dispersion of vapours escaping through a hole of intermediate size in a pressure vessel cannot yet be calculated: indeed, it is not possible to define the range of hole sizes which qualify as intermediate.

3.4 Pressurised vessel – hole in liquid space

The analysis of the escape of a liquefied gas through a hole in the liquid space introduces a number of interesting problems. If the hole is in the wall of the vessel itself (Jet 1 on Fig. 6D) it is reasonable to expect that, at least at first, the jet consists of 'unflashed' liquid which is released at a rate that may be calculated by standard methods.[17] The liquid will then flash, causing the jet to expand rapidly – blowdown experiments with pressurised steam have shown that the half-angle can exceed 90°[25] although it is not always necessarily so. The jet will then presumably continue to expand, entraining air in jet-like fashion but expanding more rapidly than is the wont of pure vapour jets (in which the half-angle is of the order of 6°)[26] because this entrained air evaporates the liquid droplets that remain after the flashing process has taken place. Once the evaporation process has been completed, the jet may be treated in conventional fashion.[26] There appear to be little data or theoretical work on the entrainment of air into unflashed or two-phase jets, so that this remains an area within which further research is needed. If the jet emerges from a long pipe (Jet 2 on Fig. 6D) there is the possibility that the vapour will flash within the pipe so that a two-phase mixture emerges into the atmosphere. Similar considerations apply to a vertical pipe such as the one leading to Jet 3. Fauske[27] has studied the methods available with which to predict whether flashing occurs within the pipe or not. For pressurised steam, it appears that flashing will occur inside the pipe if l/d (the length to diameter ratio) exceeds ten. This critical ratio depends on the thermodynamic properties of the gas in question,

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** Reproduced from Reference 23.*

† At present (October 1978) a programme of research is just beginning at SRD in which expertise accumulated as a result of many years study of the blowdown of pressurised water reactors is to be applied to the general case of the rate of release of vapour from vessels containing gas liquefied under pressure. See work by S. F. Hall,[24] in which homogeneous two-phase or multi-component mixtures discharge through a pipe.

however, and is not the same for (say) ammonia and steam†. Whether or not flashing occurs in turn affects the rate of release and, in any case, does not circumvent the lack of knowledge about the way that air is subsequently entrained into either an unflashed or two-phase jet.

Finally, a jet may emerge in such a way as to impinge on the ground or other surface (see Jet 4) and this has an important effect on the airborne liquid fraction. Resplandy[19] has shown that, for ammonia escaping from a pressurised container, allowing the jets to play onto a surface leads to the recovery of a significant part of the mass of liquid droplets that are initially airborne (he quotes 77% efficiency for a jet impinging onto the ground). There is no general prescription for calculating how the airborne liquid fraction varies with the position and orientation of the surface.

3.5 Spillage of refrigerated liquid

3.5.1 Onto land

If a tank containing refrigerated liquid should be pierced as shown in Fig. 6E, the liquid will spill into the surrounding bund and will evaporate because it is picking up heat from the ground and/or from the sun. For liquids with boiling points near or above the temperature of the ground, the influence of the wind is also important. The calculation of the rate of evaporation as a function of time is described in Reference 28, which describes the SPILL code developed at SRD. In practice, the boiling, or mass transfer processes are likely to be relatively gentle and it can be assumed that pure vapour escapes. In this case, therefore, the source for the atmospheric dispersion model is well defined. If the escaping vapour is passive, a conventional Gaussian dispersion model can be used,[15] whereas if the vapour is 'heavy' a gravitational slumping model can be coupled with the atmospheric dispersion model, as described in Section 4, or by Cox and Roe.[29]

If the spillage of refrigerated liquid is not confined by a bund, the boiling pool of liquid has a radius that increases with time (the rate of growth of radius is described by a gravitational slumping formula similar to that used for the gravitational slumping of a dense vapour, as described in Section 4) and the rate of evaporation can again be modelled using the SPILL code.[28] The source is, therefore, well defined again. For large spillages of (say) LNG this initial spread of the boiling pool means that the source for the atmospheric dispersion model may be very broad even before any subsequent vapour slumping effects are taken into account.

3.5.2 Onto or into water, Fig. 6F

For a liquid such as LNG that has no chemical interaction with the water, there is the rapid formation of a boiling pool that spreads in much the same way as it would on land. The most significant difference between this and the land case is that the rate of supply of heat per unit area to the liquid remains essentially constant since convective currents are continually bringing warm water to the surface. Here again, then, the dimensions of the source and the rate of evaporation are, in principle, well defined. If the refrigerated liquid in question is one that reacts with water, such as ammonia, some of the material will dissolve in the water. For ammonia, about 65% will dissolve if the spill occurs onto the water.[30] If the spill takes place at a distance D below the surface through a pipe of diameter d, most if not all of the ammonia dissolves if $d/D \leqslant 10$.

Some uncertainties remain unresolved, however. The boiling process can be vigorous and made even more vigorous by the heat of reaction or solution for a material such as ammonia – so that turbulence is generated. This will entrain air (note the account of Van Ulden's experiment in Section 2) and may well cause the entrainment of droplets of both water and liquefied gas. This means that it is not always possible accurately to define the source term for the atmospheric dispersion model; for example, the density could be affected in an unknown way.

3.6 Refrigerated containment – high velocity jet

If there is a small hole in a refrigerated vessel some way below the liquid surface, so that the static head is high, a jet of high velocity may emerge (see Fig. 6G). In a large ammonia-cooled

† *A. R. Edwards, private communiation*

refrigerator, for example, some of the ammonia may be both refrigerated and under pressure, so that puncturing the part of the circuit containing this ammonia will also lead to the emergence of a high velocity jet. Such a jet may well fragment; experiments with water below its boiling point, however, in circumstances in which the water was driven through holes of diameter 0·02-0·08 inches by pressures of order 80-100 psig (a static head of 100 feet of ammonia, for example, corresponds to a pressure of ~ 30 psig) shows that, while fragmentation occurs, the mean droplet diameter is 100 μ.[25] The droplet size distribution is also very sensitive to the area of the orifice, its shape and its roughness. It appears that this is another case where quantitative prediction is not yet possible.

3.7 Summary of source term discussion

In the foregoing a brief survey of a number of conceivable release modes has been given for chemically toxic and explosive gases. It should be obvious that to develop a comprehensive model, applicable to all of the circumstances in which releases may occur, is a formidable task. Certain source terms, however, have been identified as being manageable. Among these is the catastrophic failure of a pressurised vessel; interest in this sort of source has developed within SRD because one of the first tasks undertaken by the organisation in the non-nuclear field was to give state-of-the-art advice to the Health and Safety Executive's Advisory Committee on Major Hazards; the catastrophic failure of a pressurised vessel is one obvious potential major hazard. The rest of this report is devoted to a description of how to model these releases. The modelling of spillages of refrigerated liquid onto water or land is under way, as is a study of the continuous release of 'heavy', cold vapours. These will be described in forthcoming publications.

4. MATHEMATICAL MODEL FOR THE DISPERSION OF HEAVY VAPOURS

As has already been explained, there is a considerable number of mechanisms by which dense vapours can be released to the atmosphere. Consequently, there are many potential source terms, each of which affects the subsequent atmospheric dispersion of the vapour. The work described in this report, however, has been developed in the context of the study of major hazards and has, therefore, been concerned in the main with rapid releases of large quantities of toxic or explosive gases to the atmosphere. As a result, the work described in the following is intended to model 'puff' releases.

4.1 Source term

It is assumed that the vapour is at first in the form of a cylinder. The reason for making this assumption is that it is consistent with eye-witness accounts of the Potchesfstroom incident,[6] referred to in Section 2, in which some 30 Te of ammonia escaped to the atmosphere and formed an 'immediately resulting' visible cylinder some 150 m in diameter and 20 m in height. The same phenomenon was observed during an experiment, carried out in Holland, in which 1 Te of Freon-12 was poured onto water.[12] Vigorous boiling occurred, after which the mixture was roughly cylindrical in shape, of height 5-6 m and volume 2400 m^3.

It is apparent that this cylindrical source is appropriate for sudden releases from pressurised containers or when refrigerated liquid boils rapidly (e.g. LNG poured onto water). It is assumed that it is possible to specify the following parameters†:

(i) the quantity of air entrained during the formation of the cylinder

(ii) the density of the mixture in the cylinder

(iii) the initial velocity of the cylinder

(iv) the initial height and radius of the cylinder

In Reference 32, for example, the determination of the first two quantities is illustrated for catastrophic releases of ammonia from pressurised containers. Since these 'puff' releases in general generate a good deal of turbulence much air is usually entrained so that it is reasonable to assume that

† *The method of Hardee and Lee,[50] is one example of a way in which the very early development of the 'puff' can be described by taking account of the pressure energy stored in the vessel.*

the 'puff' moves with the mean windspeed at its half height. The initial height may be arbitrarily assumed to equal the radius – the rapidity with which gravitational slumping occurs means that this is not a critical assumption, (see Reference 32).

The velocity $\bar{u}(t)$ of the 'puff' at time t is given by

$$\bar{u}(t) = \bar{u}_W(10) \ln(h/2Z_0)/\ln(10/Z_0) \qquad \text{... (1)}$$

making use of the standard logarithmic formula for windspeed.[33] Here $\bar{u}_W(10)$ is the mean windspeed measured at a height of 10m, Z_0 is the meteorological roughness length and h is the vertical depth of the cloud.

4.2 Slumping

Once formed, the source cylinder begins to slump as would a column of liquid, (see Reference 12). The velocity of the edge of the cloud is adequately described by the liquid column analogy.

$$\frac{dR}{dt} = K\sqrt{(\rho - \rho_a)\, gh/\rho_a} \qquad \text{... (2)}$$

Here R is the radius, t is the time after slumping has started, ρ is the density of the mixture, ρ_a is the density of the surrounding air, g is the acceleration due to gravity and h is the height; K is a constant which has a value between unity and $\sqrt{2}$. Proof of Equation (2) by the application of Bernouilli's theorem[34] gives $K = \sqrt{2}$ while the observations in Van Ulden's experiment give $K = 1$. Unless otherwise stated, K is taken to be unity, although the user of DENZ may choose a different value. The volume V (which is not necessarily constant) is related to the radius and height by the elementary equation

$$V = \pi R^2 h \qquad \text{... (3)}$$

4.3 Cloud heating

Since there may be a temperature difference between the ground and the airborne vapour, it is necessary to consider the mechanisms by which the cloud can absorb heat.

4.3.1 Natural convection[35]

If the convection is laminar, the rate at which heat is picked up from the ground is

$$Q_c = \frac{K'_f}{L} A \left[\frac{L^3 \rho_f^2 g \beta_f \Delta T_g}{\mu_f^2} \left(\frac{C_p \mu}{K'}\right)_f\right]^{0 \cdot 25} \Delta T_g \,\mathrm{Wm^{-2}} \qquad \text{...(4)}$$

$$= \frac{K'_f}{L} A Z^{\frac{1}{4}} \Delta T_g^{\frac{5}{4}} \,\mathrm{Wm^{-2}} \qquad \text{... (5)}$$

Here C_p is the specific heat of the mixture at constant pressure,

ΔT_g is the temperature difference $T_g - T$ where T is the cloud temperature and T_g is the ground temperature

f is a subscript denoting quantities evaluated at the film temperature which is given by $(T + T_g)/2$

L is a typical dimension of the cloud

β is the volumetric coefficient of expansion of the cloud

μ is the viscosity and

K' is the thermal conductivity of the cloud

A is a constant taking a value of 0·4175, if the cloud is colder than the ground and $10^5 < Z\,\Delta T_g < 2 \times 10^7$.

If the convection is turbulent and the cloud is colder than the ground, the heating rate is given by

$$Q_c = 0{\cdot}1457 \,\frac{K'_f}{L}\, Z^{\frac{1}{3}}\, \Delta T_g^{\frac{4}{3}}\ \mathrm{Wm^{-2}} \qquad \text{...(6)}$$

The convection is turbulent if

$$3 \times 10^{10} > Z\,\Delta T_g > 2 \times 10^7 \qquad \text{... (7)}$$

4.3.2 *Forced convection*

If the local velocity difference between the cloud and the ground is V_r $\mathrm{ms^{-1}}$ the local rate of heating by forced convection is[36]

$$Q_c = f_r\, C_p\, \rho\, V_r\, \Delta T_g \qquad \text{... (8)}$$

where f_r is a friction factor. This contribution has been neglected in this report.

4.3.3 *Heating by the Sun*

In principle, the cloud may be heated by the Sun, assuming that it is daytime. The rate at which heat is absorbed depends on what the cloud consists of and whether it absorbs radiation strongly. A dry ammonia-air mixture, for example, is virtually transparent to the spectrum of the sun's radiation.

The simple model described in this report, therefore, incorporates heating by the ground due to turbulent natural convection and neglects any other source of heat. The rate of increase of temperature is given by

$$\frac{dT}{dt} = \frac{\alpha\,(\pi R^2)\,\Delta T_g^{\frac{4}{3}}}{m_a C_{pa} + m_g C_{pg}} \qquad \text{...(9)}$$

where those symbols not already defined are as follows:

α is the coefficientof $\Delta T_g^{\frac{4}{3}}$ in Equation (6), and

m is the mass and C_p the specific heat at constant pressure of air (a) or the toxic or explosive gas (g).

4.4 Entrainment of air

In practice, air will be entrained both at the edges of the cloud and at the top. For edge entrainment during slumping,

$$\frac{dm_a}{dt} = 2\rho_a\, \pi\, Rh\, \alpha^* \frac{dR}{dt} \qquad \text{... (10)}$$

where α^* is a constant to be determined empirically. Van Ulden,[12] for example, claims that his results are consistent with $\alpha^* = 0$; recent experiments carried out at Porton,[14] in which about 100 kg 'puffs' of Refrigerant-12 were released, suggest that $\alpha^* \neq 0$. The magnitude of α^* for large scale releases remains uncertain, therefore. A default value of zero is assumed for α^* in the program DENZ, though the user may specify another value if desired.

The calculation of the rate of entrainment over the top surface is not yet possible, given the present state of theoretical knowledge; there are, however, suggestions current in the literature. Germeles and Drake[36] define an entrainment velocity which is proportional to the local velocity difference over the top surface. The presence of this velocity difference means that mechanical turbulence is generated. This mechanism is clearly important when there are large local velocity differences. If, however, the velocity difference is small, the ambient turbulence assumes a dominant role. The entrainment velocity U_e should then be dependent on some form of the Richardson number Ri. Cox and Roe,[29] for example, suggest that

$$U_e = \alpha' U_l Ri^{-1} \qquad \text{... (11)}$$

where

$$Ri = (g l_s / U_l^2)\, \Delta \rho / \rho_a \qquad \text{... (12)}$$

Equation (11) is valid when $U_e \ll U_l$. U_l is the longitudinal turbulence velocity which is proportional to the friction velocity u_* with the constant of proportionality being 3·0 (very unstable, category A-B weather), 2·4 (neutral, category C-D weather) or 1·6 (very stable, category E-F weather).[29] These values are used in DENZ. α' is an entrainment constant which has a default value of 0·5. The choice of a characteristic length l_s is not certain, but here l_s is the turbulence length scale which is a function of the height above the ground of the stability. An expression for l_s as a function of h is given by Taylor et al[37] (very roughly, $l_s(h) \propto h^{\frac{1}{2}}$ in neutral stability). If the model of Cox and Roe is assumed, the rate at which air is entrained into the cloud is given by

$$\frac{dm_a}{dt} = \rho_a (\pi R^2) U_e + 2\rho_a \pi R h \alpha^* \frac{dR}{dt} \qquad \text{... (13)}$$

At the same time, Equation (9) must be modified so that

$$\frac{dT}{dt} = \frac{\frac{dm_a}{dt} C_{pa} \Delta T_a + \alpha (\pi R^2) \Delta T_g^{\frac{4}{3}}}{m_a C_{pa} + m_g C_{pg}} \qquad \text{... (14)}$$

where ΔT_g, the difference in temperature between the ground and the cloud, does not necessarily equal ΔT_a, the temperature difference between the air and the cloud. The rate of growth of the radius is still given by

$$\frac{dR^2}{dt} = 2K \sqrt{\frac{g(\rho - \rho_a)V}{\pi \rho_a}} \qquad \text{... (15)}$$

(which is merely Equation (2) rewritten).

Two additional equations are required

$$\rho = \frac{[m_a + m_g]}{[m_a/\rho_a + m_g/\rho_g]} \cdot \frac{T_a}{T} \qquad \text{... (16)}$$

and

$$V = [m_a + m_g]/\rho \qquad \text{... (17)}$$

It follows that m_a, T and R^2 are the only independent variables in the three coupled linear differential Equations (13) - (15), which may be solved numerically.

4.5 Transition to a passive plume

The computer program DENZ uses two alternative tests to determine whether the plume may be deemed to be passive. It first tests to see whether both of the following conditions are satisfied (i) The gravitational slumping must cause a rate of increase of radius not exceeding that to be expected by the atmospheric turbulence alone, that is, it asks the question, is

$$\frac{dR}{dt} = K\sqrt{(\rho-\rho_a)\,gh/\rho_a} < 2{\cdot}14\,\frac{d\sigma_y(x)}{dt}\,, \qquad \text{... (18)}$$

(making the conventional assumption that the radius is at the 10% edge of a Gaussian profile). Conventional parameterisations of the rate of lateral spread of a plume[38] give

$$\frac{d\sigma_y(x)}{dt} = C^{*}\,\frac{dx}{dt} = C^{*}\bar{u} \qquad \text{... (19)}$$

where C^* depends on the stability category and $\bar{u}$ is the velocity of the 'puff'. C^* takes on the values 0·22, 0·16, 0·11, 0·08, 0·06 and 0·04 in Category A, B, C, D, E and F weather, respectively. (ii) As $Ri \to 0$, U_e should become equal to U_1, although the functional form of the way in which U_e approaches U_1 is not known. The computer program assumes that Equation (11) holds and tests for

$$U_e > U_1 \qquad \text{... (20)}$$

If Equations (18) and (20) are both valid, transition is made to a passive plume model.

Meanwhile, the density difference $\Delta\rho$ is also calculated and if $\Delta\rho < 1{\cdot}0 \times 10^{-3}$ kgm^{-3} it is assumed that the plume becomes passive even if Equations (18) and (20) are not satisfied. The critical value of$\Delta\rho$ can be varied by the user.

It is frankly admitted that the above prescriptions are purely artificial; however, there appears to be no well established method for determining when the transition should occur. It is to be hoped that large scale experimental releases of Refrigerant-12 in the open air (for which a feasibility study is under way at Porton)[40] will throw light onto this problem.

Suppose that the transition occurs at a point x_t downwind of the source and that the height and radius are then h_t and R_t respectively. It is assumed that the concentration distribution within the 'puff' is Gaussian so that effective longitudinal, lateral and vertical standard deviations may be defined as follows

$$\sigma_{zt} = h_t/2{\cdot}14 \qquad \text{... (21)}$$

and

$$\sigma_{xt} = \sigma_{yt} = R_t/2{\cdot}14 \qquad \text{... (22)}$$

At greater distances downwind, the variances become

$$\sigma_z^2(x) = \sigma_{zt}^2 + \sigma_{zh}^2(x-xt) = (h/2{\cdot}14)^2 \qquad \text{... (23)}$$

$$\sigma_y^2(x) = \sigma_x^2(x) = \sigma_{yt}^2 + \sigma_{yh}^2(x-xt) = (R/2{\cdot}14)^2 \qquad \text{... (24)}$$

where σ_{zh} and σ_{yh} depend on the weather category and are calculated according to the prescription gven by Hosker.[38]

4.6 Concentrations within the 'puff'

If a total quantity m_g of toxic or explosive material is released, the assumption is made in DENZ that the material is distributed in a Gaussian fashion across the 'puff' (this is not logically consistent with the use of the slumping formula, Equation (2), but to within the accuracy expected of the model it is not an unreasonable assumption; see Reference 32). At any point (x, y, z) and at time t the air-borne concentration is given by

$$\chi(x,y,z,t) = \frac{m_g\, G(x,y,z,t)}{\sqrt{2}\,\pi^{\frac{3}{2}}\sigma_y^2\sigma_z} \qquad \text{... (25)}$$

where

$$G(x,y,z,t) = \exp\left(-(y^2 + (x - x(t))^2)/2\sigma_y^2 - z^2/2\sigma_z^2\right) \qquad \text{... (26)}$$

and x (t) is the position of the 'puff' centre point at time t.

$$x(t) = \int_0^t \bar{u}(t')\,dt' \qquad \text{...(27)}$$

The standard deviations are given by $\sigma_y = R/2{\cdot}14$ and $\sigma_z = h/2{\cdot}14$ for all values of x.

Equations (1) - (27) form the basis of the model programmed into DENZ; the calculations that it carries out are described in the next section.

4.7 Validity of the model

The simple model discussed in the foregoing suffers from the same drawback as the models of other authors, whether these attempts to condense the relevant physics into a few simple equations similar to Equations (13) - (17)[24,36] or whether they attempt a more sophisticated numerical analysis.[41,42] This is that the models are intended for the prediction of the spillage of large (1 - 1,000 Te +) quantities of hazardous gases, yet unfortunately there are no experimental data available in this mass range with which to compare the model. As a result, the predictions given by different authors can vary considerably. Havens, for example, has reviewed methods for calculating the consequences of the spillage of 25,000 m^3 of LNG onto water and finds that predictions of the hazard range (that is, the distance within which the cloud could be ignited by a spark or flame) vary from 0·75 miles to 50 miles.[43] There are several reasons why this is so, but the single most important difference between the various models lies in the choice of the mechanism for entrainment of air analagous to Equation (13). It seems likely that the correct choice of entrainment mechanism will not be settled until large scale experiments have been carried out. Plans for at least two such series of experiments are being made. It is proposed to release up to 80 Te of ammonia from pressurised tanks at a site in the USA[44] and a feasibility study for 'puff' releases of 5 - 10 Te of Refrigerant-12 is being carried out at Porton in the UK.[40] The US Department of Energy has also prepared a comprehensive review of the theoretical and experimental work necessary for the development of methods for predicting the consequences of large scale releases of LNG.[45]

Meanwhile, what confidence can the user have in the simple model described in the foregoing? This question has already been thoroughly discussed in References 32 and 46. It appears that the use of the slumping formula in Equation (2) is well proved. It has been used as a successful element of a model for the release of about 100 kg 'puff' mixtures of air and Freon,[14] and describes the evolution of the 1 Te Freon-12 release carried out by Van Ulden.[12] Furthermore, in Reference 46 it is compared with the observed consequences of four accidental releases of ammonia from pressurised containers. The quantities released were 19 Te,[5] 38 Te,[6] ~ 40 Te[3] and 76 Te[7] and each of these incidents provides evidence for the validity of Equation (2). For example, the 40 Te release which took place at Pensacola in November 1977[3] was observed to form a vapour cloud that, after four minutes or so, was 'about a mile across'. This is in good agreement with the predictions of the model.

The prediction for the rate of cloud heating by the ground, given in Equation (6), is a well established correlation.[35] There do not exist detailed temperature measurements within a large, cold, 'heavy' vapour cloud against which the model can be checked but it is anticipated that this will not prove to be a prediction on which the validity of the model depends crucially.

As has already been mentioned, it is the prediction for the rate of entrainment of air, Equation (13), that gives rise to the greatest uncertainties. Reference 29 reviews the reasons for the choice of Equation (13), which is based on experiments in which a lighter fluid was injected over a denser one. Reference 29 also explains how a model incorporating Equation (13) is in good agreement with the observed results of tests by the American Gas Association[47] in which LNG vapour was evolved at rates up to about 20 kgs^{-1}.

Once slumping has terminated and the ambient atmospheric turbulence starts to work on the cloud, predictions of the height, h, are extremely sensitive to the assumed rates of entrainment of air. For the 40 Te release of ammonia, mentioned above, which took place at Pensacola, the observed height of the cloud when it was about a mile across was 40 m. Reference 46 explains that this is in good agreement with the model predictions. It is concluded that, given the present scanty state of experimental knowledge, the model can be deemed to be successful. In view of the uncertainties identified at various stages in the previous sections of this report, however, it is apparent that the work reported here is by no means the last word upon the subject. It should merely be regarded as a promising step towards the development of a 'complete' model.

The program DENZ has been written in such a way that it will be easy to incorporate future prescriptions for cloud heating and the entrainment of air. In principle, extra differential equations taking account of other phenomena, such as the occurrence of chemical reactions within the plume, may easily be added. In addition, work is under way at SRD in which some of the other source terms identified in Section 2 are to be studied. The possibility of embarking on a programme of more detailed numerical modelling is also being examined.

4.8 Simplified model

To digress somewhat from the main considerations of this report, in the early stages of the development of the model it became apparent that the atmospheric dispersion of a 'puff' containing cold, 'heavy' vapour could conveniently be divided into four stages; these have been deduced by reference to Van Ulden's experiment.[12]

4.8.1 Stage 1

This corresponds to the formation of the source cylinder, as described in Section 4.1.

4.8.2 Stage 2 'Slumping'

Once the source cylinder has stabilised it begins to slump with very little entrainment of air (see Reference 12). The growth of the radius is described by Equation (2). In time, however, the entrainment of air must become important and slumping must cease. Van Ulden's requirement for the termination of slumping is that buoyancy induced velocities (which, from Equation (2) are proportional to $\sqrt{\Delta\rho h}$) should be comparable to the rate of spread of the cloud due to the action of atmospheric turbulence, i.e. should be proportional to u_*, the friction velocity. u_* is given by the equation

$$\bar{u}_W(10) = \frac{u_*}{k} \ln\left(\frac{10}{Z_0}\right) \qquad \text{... (28)}$$

where k is Von Karman's constant (k ~ 0·4) and Van Ulden's criterion for termination of slumping is

$$\frac{\Delta\rho g h}{\rho_a u_*^2} = 4 \qquad \text{... (29)}$$

Sometimes this prediction can lead to ridiculously small heights of slumping (fractions of a centimetre) and it is convenient to introduce the concept that slumping terminates at a height comparable to that of the roughness elements on the surface – this height can be chosen by the user of DENZ.

4.8.3 *Stage 3 'Ground hugging'*

In this simplified approach, entrainment of air begins once slumping has terminated. The rate of increase in height is much smaller than that expected from the action of the ambient turbulence – it is only about a third of that to be expected in Pasquill Class F (highly stable) weather conditions, whereas the category actually observed during the Freon-12 experiment was D to E. In SRD's original simplified model it was assumed that this rate of increase in height is valid, irrespective of the weather conditions. The radius meanwhile continues to grow as predicted by Equation (2).

The existence of these three stages is illustrated in Figs. 8 and 9, which are taken from Van Ulden's work.[12]

4.8.4 *Stage 4*

When the density difference $\Delta\rho$ is small enough, all density driven effects disappear and the rate of growth of the 'puff' is determined by the ambient atmospheric turbulence alone. A conventional Gaussian dispersion model can then be used.[15] $\Delta\rho \sim 0{\cdot}001$ kg m^{-3} (or a value set by the user) defines the transition point between Stage 3 and Stage 4.

This simple four stage model is still programmed into DENZ and can be chosen by the user if he/she wishes. It has been left there because it is believed that this qualitative picture of four stages is a useful one. Some of the terminology used in the output of DENZ is only meaningful when seen against this background of the program's development.

5. CALCULATIONS CARRIED OUT BY DENZ

This section is devoted to a description of the way in which Equations (1) - (27) are made use of in DENZ, and the calculations that it carries out.

As with any other computer program, the user must provide certain input information and the control cards necessary for this are described in Section 6. The calculation starts with the source cylinder. The user must provide the mass of gas and the mass of air within the cylinder together with its initial density and temperature. The ratio of height h_0 to radius R_0 must also be specified (a default value of unity is assumed). Finally, the value of the windspeed $\bar{u}_W$ (10) must also be given. In practice the user must specify how many different weather conditions he/she wishes to consider, where a weather condition is defined by a knowledge of the weather category and the windspeed. By default, the whole spectrum of possible weather is divided into seven conditions as described in Table 1, but the user may define up to twenty four category-windspeed pairs.

The definition of the characteristics of the source cylinder and of the weather enables DENZ to begin its calculations. These differ slightly depending on whether a gas is toxic or explosive.

5.1 Toxic gases

5.1.1 *Approximate calculations*

The average concentration $\bar{C}_f(\tau)$ required to kill a person is in general a complicated function of the exposure time τ. The same is true of the average levels of concentration required to produce other effects such as serious illness or irritation. Figure 10, for example, which has been taken from Reference 48, shows how the lethal exposure time τ for chlorine varies with average concentration $\bar{C}(\tau)$. Figure 10 may roughly be described by the equation[49]

$$\tau\left[\bar{C}_f(\tau)\right]^{-2{\cdot}3} = \text{constant} \qquad \dots (30)$$

In DENZ, the user is required to provide the $\bar{C}(\tau)$ vs. τ curve as an array of numbers for interpolation.

If $\bar{u}$ and σ_y do not change very much as a cloud passes by a fixed point at ground level, (x, y, o), the quantities τ and $\bar{C}(\tau)$ are easily calculated to be

$$\tau(x) = 4{\cdot}28\,\sigma_y(x)/\bar{u} \qquad \dots (31)$$

with

$$\bar{C}(\tau(x), y) = \frac{m_g \exp(-y^2/2\sigma_y^2)}{4{\cdot}28\pi\sigma_y^2\sigma_z} \quad \text{... (32)}$$

It is these quantities that DENZ calculates as a function of distance downwind. In order to limit the number of calculations required, they are performed at a limited number of 'grid points' defined as follows. Suppose that the maximum range in which the user is interested is r_d (which he either provides himself or takes to have a default value of 10 Km), then the range r_d is divided into 48 intervals equally spaced in lnx with an interval given by

$$\text{int} = 1{\cdot}5\,(\ln r_d/49) \quad \text{... (33)}$$

where the factor 1·5 is chosen arbitrarily to ensure that the one dimensional computational grid so established extends comfortably beyond r_d. The position of the j^{th} point on the grid is

$$x_j = \exp((j-1)\,\text{int})\ \text{metres} \quad \text{... (34)}$$

with

$$x_1 = 1\ \text{metre} \quad \text{... (35)}$$

The program then calculates and prints out the following quantities for each value of j; x_j, R, $\tau(x_j)$, $\bar{C}(\tau(x_j), 0)$, and $t(x_j)$ where $t(x_j)$ is the time taken to reach x_j. It also prints out the cloud temperature T, the average density ρ, the density difference Δρ, the rate at which heat is being supplied through the base of the cloud, the mass of air in the 'puff' m_a, the entrainment velocity U_e, and the Richardson number Ri from Equations (11) and (12).

At each grid point the calculated value of $\bar{C}(\tau(x_j), 0)$ is compared with the input information on the value of $\bar{C}$ actually required to cause death, or whatever other consequence is being considered, $\bar{C}_f(\tau(x_j))$. When $\bar{C}(\tau(x_j), 0)$ falls below $\bar{C}_f(\tau(x_j))$, values of the $\bar{C}$'s are linearly interpolated between that and the previous grid point to obtain an approximate estimate of the hazard range x_h.

If this value x_h lies just beyond x_n, then for all grid points closer to the origin the quantity y_j is calculated by solving the equation

$$\bar{C}_f(\tau(x_j)) = \bar{C}(\tau(x_j), 0)\, e^{-y_j^2/2\sigma^2(x_j)} \quad \text{... (36)}$$

An estimate of the area above which concentrations of gas above the given level are to be found is given by

$$A_h = \sum_{j=1}^{n-1} (x_{j+1} - x_j)(y_{j+1} + y_j) + y_n(x_h - x_n) \quad \text{... (37)}$$

If these estimates are considered to be sufficiently accurate, the calculation may be terminated at this point and will prove to be most economical in terms of computer time. If greater accuracy is required (in particular, a consideration of slumping behind the source) DENZ goes on to carry out a more sophisticated numerical calculation.

5.1.2 Accurate calculation of ranges and areas

DENZ computes $\bar{C}(\tau_j)$ and $\bar{C}(\tau(x_j), 0)$ numerically at each downwind grid point without assuming (as in Equation 32) that σ_y and $\bar{u}$ do not change as the cloud passes by, and hence determines the smallest value of x_j at which $\bar{C}(\tau(x_j)\,0)$ is less than $\bar{C}_f(\tau(x_j))$. The hazard range, x_h, is then found by calculating $\bar{C}(\tau(x'), 0)$ at points between x_j and x_{j-1}, and determining the value of x', $(x_{j-1} \leqslant x' \leqslant x_j)$, such that,

$$\bar{C}(\tau(x'), 0) < \bar{C}_f(\tau(x'))$$

and

$$\bar{C}(\tau(x'-10), 0) \geqslant \bar{C}_f(\tau(x'-10)), \quad \text{...(38)}$$

i.e. the value of x_h is determined to within 10 m.

Values of $\bar{C}(\tau(x'), 0)$ are found using a logarithmic interpolation between the values of concentration and cloud radius at the jth and (j−1)th grid point.

A similar calculation is performed to determine the upwind hazard range.

The downwind area within which hazardous concentrations may occur is found by first determining the crosswind distance, y_j, at each grid point, at which the following expressions are valid,

$$\bar{C}(\tau(x_j), y_j) < \bar{C}_f(\tau(x_j, y_j))$$

and

$$\bar{C}(\tau(x_j), y_j - 10) \geqslant \bar{C}_f(\tau(x_j, y_j) \quad \text{... (39)}$$

where $\bar{C}_f(\tau(x_j, y_j))$ is the average concentration considered hazardous if inhaled over a time period greater than or equal to the duration of cloud passage at point (x_j, y_j). The value of this duration is found by estimating the difference between the time of arrival of the leading 10% edge of the cloud and the time of the departure of the trailing 10% edge, again making no assumptions about the constancy of σ_y or $\bar{u}$ during the passage of the cloud. Thus, the duration of the cloud passage off-axis is not the same as on the axis so that the method described here is a refinement of that used in Equation (36).

The downwind hazard area is then calculated using Equation (37).

A similar calculation is performed for the upwind hazard area.

5.1.3 Interaction with the population

The scheme described so far enables the user to determine, for a number of weather conditions, whether or not the hazard level under consideration is exceeded at any point. In order to calculate the effect on the surrounding population it is necessary to provide simplified population data and weather data as described in Fig. 11.

Twelve sectors are defined; the first from 0 - 030°, the second from 030 - 060° and so on. If the wind blows into one of these sectors it is assumed to do so along the centre-line; that is, it is supposed that there are twelve discrete wind directions along the lines labelled 1, 2, ..., 12. From weather statistics available from Meteorological Stations it is possible to compile a table of joint probability distributions p (i, CAT, u) where i specifies the sector into which the wind is blowing, CAT labels the weather category, and $u = \bar{u}_W(10)$.

The population data are then simplified as follows. The user chooses radii r_1', r_2', r_3' ... out to some maximum r_m'. For each of the twelve thirty degree sectors, all the people living between r_1' and r_2' are assigned to a radius $r_1 = (r_1' + r_2')/2$; those between r_2' and r_3' to $r_2 = (r_2' + r_3')/2$ and so on out to a maximum radius (already encountered) $r_d = (r_{m-1}' + r_m')/2$. The people assigned to a given radius and sector are then spread uniformly across an arc; or more precisely are assigned to seven points spread across the thirty degree sector. This is shown on Fig. 11 where there are 12 x 7 = 84 equally spaced dots on the r_3 circle. All other circles r_1, r_2 ... r_d are similarly divided.

Suppose now that the wind blows into Sector 1. DENZ begins with r_1 and moves around all 84 population points, determining for each one whether it is inside or outside the part of the cloud within which airborne dosages are above the hazard level. For small radii and a large slumping cloud, all of the circle could, in principle, be so affected. The process is repeated for succeeding radii and the number of people at risk from the specified release summed.

The calculation can be repeated for the other sectors, and for all the weather conditions defined as input to the program. In other words, associated with each conditional probability p (i, CAT, $\bar{u}_W$) there is a number N (i, CAT, $\bar{u}_W$) of people at risk of death, or of illness, or of whatever other consequence is being considered. DENZ sorts these numbers into ascending values of N and cumulative probabilities to give $P_c - N$ lines, that is, plots of the probability P_c, conditional on the release taking place, with which N or more people are put at risk. If the frequency, f, with which the release takes place has been estimated, the P_c–N lines can be converted into so-called f-N lines which are a convenient way of summarising the societal risk.

5.2 Explosive gases

The user of DENZ must supply certain hazard levels (e.g. the LFL, L_f). These refer to hazardous levels of instantaneous concentration rather than dosage, so that DENZ cannot treat explosive gases in the same way as it does toxic ones.

5.2.1 Approximate calculations

At any time t the centre of the 'puff' is at position x (t), moving with velocity $\bar{u}$ (t). The cloud centre line concentration is

$$\chi(x(t), 0, 0, t) = \frac{m_g}{\sqrt{2}\,\pi^{\frac{3}{2}}\,\sigma_y{}^2\,\sigma_z} \qquad \ldots (40)$$

DENZ works out χ (x (t), 0, 0, t) and, if the n^{th} grid point is the one at which this first falls below L_f, it interpolates linearly between x_n and x_{n-1} to solve the equation for the hazard range x_h.

$$\chi(x_h, 0, 0, t(x_h)) = L_f \qquad \ldots (41)$$

For each grid point closer to the origin, the equation,

$$\chi(x_j, y_j, 0, t(x_j)) = L_f \qquad \ldots (42)$$

is also solved for y_j, the radius of the hazardous cloud.

Equation (37) may then be used to give an approximate estimate of the area A_h within which an ignition source could set the cloud on fire.

5.2.2 Accurate calculation of ranges and areas

The hazard range and area are found more accurately by first solving Equation (42) in order to find the cloud radius, y_j, within which L_f is exceeded when the cloud centre is at x_j. The crosswind distance, y_i, to L_f is then determined at each downwind grid point, x_i from,

$$y_i = \max\left(\sqrt{y_j{}^2 - (x_j - x_i)^2}\right) \qquad j = 1 \ldots 48 \qquad \ldots (43)$$

and the downwind hazard range, x_h, from

$$x_h = \max(x_j + y_j) \qquad j = 1 \ldots 48,\ y_j > 0 \qquad \ldots (44)$$

The downwind hazard area is then calculated using Equation (37) and performing the summation over i instead of j.

A similar calculation is performed to find the upwind hazard range and area.

5.2.3 *Interaction with the population*

For flammable gases, the program does **not** go on to calculate how many people might be within A_h since these are not the only people who would be at risk from combustion, detonation, or deflagration of the 'puff' – pressure waves or radiant energy could affect people outside this area. The extension of the DENZ methodology to cover the consequences of igniting the cloud is a project for the future.

6. INPUT AND CONTROL CARDS AND DEFAULT VALUES

The input and control cards necessary to run DENZ are described in this section under the following headings:-

(i) Title cards

(ii) Compulsory input cards

(iii) Optional control cards

(iv) Cards ending a run of DENZ

The user of DENZ is able to select from a great many different types of calculations. This selection is made by means of instructions to the program via key words. Unless otherwise stated all key words are in A8 format and are left justified, all numbers are in E10.3 format and are right justified. Columns 9 and 10 are blank on most control cards.

Throughout this section the following symbols will be used:

_ to indicate a blank column

( ) to indicate a group of ten blank columns

| | to enclose a group of ten columns

6.1 Title cards

Each new run of DENZ must start with one or more title cards. The first four columns of each card must not be left blank; anything appearing in these columns will be ignored. All characters appearing in the remaining 76 columns will be treated as part of the title and reproduced, verbatim, at the beginning of the output.

After the last title card there must be one blank card.

6.2 Compulsory input cards

The following cards are compulsory. They may appear in any order.

6.2.1 *The AIR card*

AIR	m_{ao}	ρ_a	( )	( )	( )	( )	( )

This card specifies the mass of air, m_{ao} kg, initially mixed with the released gas to form the source cylinder, and the density of air, ρ_a kgm^{-3}, at ambient temperature.

6.2.2 *The GAS card*

GAS	m_g	ρ_o	T_o	( )	( )	( )	( )

m_g is the mass of gas released, in kg, and ρ_o is the initial density of the air-gas mixture, in kgm^{-3} (i.e. the density of the source cylinder). Similarly, T_o is the initial temperature (K) of the air-gas mixture.

6.2.3 The HAZARD card

HAZARD	nhaz	ntype	( )	( )	( )	( )	( )	

This card specifies the nature of the hazard presented by the released material. nhaz ($\leqslant 3$) is the number of different hazard levels to be considered, e.g. death or illness for toxic gases and U.F.L. or L.F.L. for flammable material etc. ntype is a control index determining the type of hazard, it should be set to one for toxic gases and two for flammable gases. The cards described below are then required:

ntype = 1

nhaz groups of cards as follows:

(i) one card, in I3 format, giving the number of times, n_t ($\leqslant 50$), at which the hazardous concentration of gas and corresponding exposure time are to be specified in order to provide DENZ with information such as is contained in the chlorine exposure plot on Fig. 10.

(ii) A card, or cards, in 8E10.3 format, containing n_t hazardous concentration levels (kg/m^3) in descending order.

(iii) A card, or cards, in 8E10.3 format, containing n_t exposure times, in seconds. The ith of these exposures times must correspond to the ith hazardous concentration level given on the previous card.

ntype = 2

One card, in 8E10.3 format, containing nhaz values of the hazard level, in kg/m^3; e.g. upper and lower flammable limits.

6.3 Optional control cards

The following cards are optional and may appear in any order. The effect of omitting any of these cards is described in Section 6.5.

6.3.1 The ALL card

ALL	( )	( )	( )	( )	( )	( )	( )

If this card is used then output is produced for all weather categories/velocity subdivisions.

6.3.2 The AREA card

AREA	a	( )	( )	( )	( )	( )	( )

This card specifies the base area, a metres^2, of the source cylinder.

6.3.3 The CUT_OFF card

CUT_OFF	h_c	( )	( )	( )	( )	( )	( )

h_c is the height, in metres, of the cloud at the termination of the slumping phase, assuming that the simplified model of Section 4.8 is being used. It may be considered as the height of typical roughness elements on the ground.

6.3.4 The ENTRAIN card

ENTRAIN	ent	T_a	α^*	α'	( )	( )	( )

ent is an entrainment index which should be set to one for selection of the Cox and Roe model (Equations (13) - (14)). The temperature of the air, in Kelvin, is specified as T_a, α^* and α' are the proportionality constants governing edge and top entrainment, respectively (see Equations (10) and (11)).

If ent is set to zero then it is assumed that there is no entrainment of air during the slumping process; the rate of growth of the cloud radius is then given by Equation (2). Columns 20-80 of the card should be left blank.

6.3.5 The F-NLINES card

F-NLINES	( )	( )	( )	( )	( )	( )	( )

For toxic gases only, cumulative probability/number of casualty tables for each of the nhaz hazard levels specified by the HAZARD card will be produced if this card is used; see Section 5.1.3.

6.3.6 The HEAT card

HEAT	α	C_a	C_g	T_a	ρ_g	( )	i

This card specifies that cloud heating by the various mechanisms described in Section 4.3 is to be considered. i is a control index which should be set to one if the user wishes to supply values for the ground temperature in the various weather categories/velocity subdivisions. If i is set to one then this card must have been preceded by the WEATHER card, if that card is to be used, and must be followed by further cards containing data on ground temperatures, in Kelvin, where the ith number on the jth card refers to the temperature of the ground in the ith velocity sub-division of the jth Pasquill stability category (A = 1, B = 2 ... F = 6), as defined either by the WEATHER card or by the default weather data (Table 1).

α is the constant in the equation for heating by turbulent natural convection (Equation (9)), C_a and C_g are the average specific heat capacities ($Jkg^{-1} K^{-1}$) of air and the released material, respectively, T_a is ambient temperature (K), and ρ_g is the density (kgm^{-3}) of the released material at ambient temperature.

6.3.7 The HEIGHT card

HEIGHT	z_r	( )	( )	( )	( )	( )	( )

Wind speeds given either by the WEATHER card or by the default weather data are assumed to be measured at a height of z_r metres.

6.3.8 The RANGE card

RANGE	( )	( )	( )	( )	( )	( )	( )

If this card is used then the range and corresponding area within which the concentration exceeds the levels specified on the HAZARD card are calculated by the method described in Section 5.1.2.

6.3.9 The ROUGHNESS card

ROUGHNESS	Z_o	( )	( )	( )	( )	( )	( )

The surface roughness length is Z_o metres.

6.3.10 The SITE card

SITE	n_r	n_s	( )	( )	( )	( )	( )

This card is used to define the population distribution around the site. It is necessary to define the number of radii, n_r ($\leqslant 20$), and the number of sectors, n_s, ($1 < n_s \leqslant 12$), in the distribution; the following data are then required.

(a) A card, or cards, giving n_r values for the radii, in metres, at which calculations are to be performed. The radii should be in order of increasing magnitude.

(b) $n_r \times n_S$ numbers giving the number of people at each radius in each sector. The order in which these numbers appear is important – starting at the smallest radius specify the number of people, n, in each sector, i.e. n (1,i) for $i = 1, n_S$. Repeat this process for each successive radius, i.e. define n (j,i) for $i = 1, n_S$ and for $j = 1, n_r$, by altering first i and then j.

6.3.11 The STAGE_3 card

STAGE_3	Δρ	( )	( )	( )	( )	( )	( )

This card defines the centre line concentration density difference, Δρ, kgm^{-3}, at which Stage 3 of the cloud's dispersion is assumed to be complete; that is, the density difference for which transition to passivity takes place.

6.3.12 The VAN_ULDEN card

VAN_ULDEN	K	( )	( )	( )	( )	( )	( )

K is the value of the constant in Van Ulden's formula for the rate of growth of the cloud radius (Equation (2)).

6.3.13 The WEATHER card

WEATHER	n_1	n_2	n_3	n_4	n_5	n_6	( )

This card defines the weather conditions around the site. The number of velocity subdivisions in each Pasquill stability category are specified by n_1 to n_6, ($n_i \leqslant 4$), where n_1 refers to Category A, n_2 to Category B .... n_6 to Category F. The following data are then required.

(a) On a new card, n_1 numbers corresponding to the velocity subdivisions, in m/s, appropriate to the 1st weather category (A). Repeat for each weather category for which $n_i > 0$.

(b) For weather category A and the first velocity subdivision, n_S numbers are required. The kth number is the probability that the wind blows **into** the kth sector of the population distribution with that wind velocity and in that weather category. Starting on a new card each time repeat for the remaining weather category/velocity pairs, i.e.

$(A,2)..(A,n_1),(B,1)..(B,n_2),...(F,n_6).$

Note that these probabilities are normalised by DENZ.

6.4 Cards ending a run of DENZ

The following cards are compulsory.

6.4.1 The CONTINUE card

CONTINUE	( )	( )	( )	( )	( )	( )	( )

Further runs of DENZ may be initiated by this card. It should be followed by the title and control cards described in earlier sections. Any new data following this card will overwrite all values set on previous similar data cards.

6.4.2 The END card

END	( )	( )	( )	( )	( )	( )	( )

This card is used to define the end of a data block. If further runs are required then it should be followed by the CONTINUE card, otherwise it should be followed by another END card (i.e. the complete set of data is terminated by two END cards), in which case control within DENZ jumps to the STOP instruction.

A summary of the control cards appears in Table 2.

6.5 Default values

The effect of omitting each optional control card is described in this section.

6.5.1 ALL

Output is produced for Pasquill stability Category A – first velocity subdivision, Pasquill stability Category B – first velocity subdivision, Pasquill stability Category D – second velocity subdivision, and Pasquill stability Category F – first velocity subdivision. The numbering of the velocity subdivision is either that given in the data following the WEATHER card (if present) or is taken from the default weather data described later in this section.

6.5.2 AREA

The initial base area of the cloud is calculated from the assumption that the base is circular and of radius equal to the height of the cloud. The initial volume of the cloud is determined from knowledge of its initial mass and density.

6.5.3 CONTINUE

No further runs are performed.

6.5.4 CUT_OFF

Stage 2 is terminated when the height of the cloud either falls below 0·5 metres or Van Ulden's limit, see Equation (29), whichever is the greater.

6.5.5 ENTRAIN

Cox and Roe entrainment model is used. The temperature of the air is taken as 293 K, α^* (Equation (10)) is assumed to be zero, i.e. there is no edge entrainment, and α' (Equation (11)) is 0·5. The ground temperature is equal to the air temperature.

6.5.6 F-NLINES

The probability/number of casualty calculations are not performed.

6.5.7 HEAT

The heating of the cloud by any of the methods described in Section 4.3 is not considered.

6.5.8 HEIGHT

Input wind speeds are assumed to be measured at a height of 10 metres.

6.5.9 RANGE

The range and corresponding area within which the concentration exceeds the levels specified on the HAZARD card by the user of DENZ are only calculated approximately.

6.5.10 ROUGHNESS

A surface roughness length of 10 cm is assumed.

6.5.11 *SITE*

A 12 sector population distribution is used which consists of 1 person in each sector and at each of the radial points given by,

radius = 500 x n − 250 metres   where n = 1 to 20.

6.5.12 *STAGE_3*

Stage 3 of the dispersion process is assumed to be terminated when the centre-line density difference, $\Delta\rho$, falls to 0·001 kg/m³.

6.5.13 *VAN_ULDEN*

Constant, K, in Equation (2) is assumed to be 1.

6.5.14 *WEATHER*

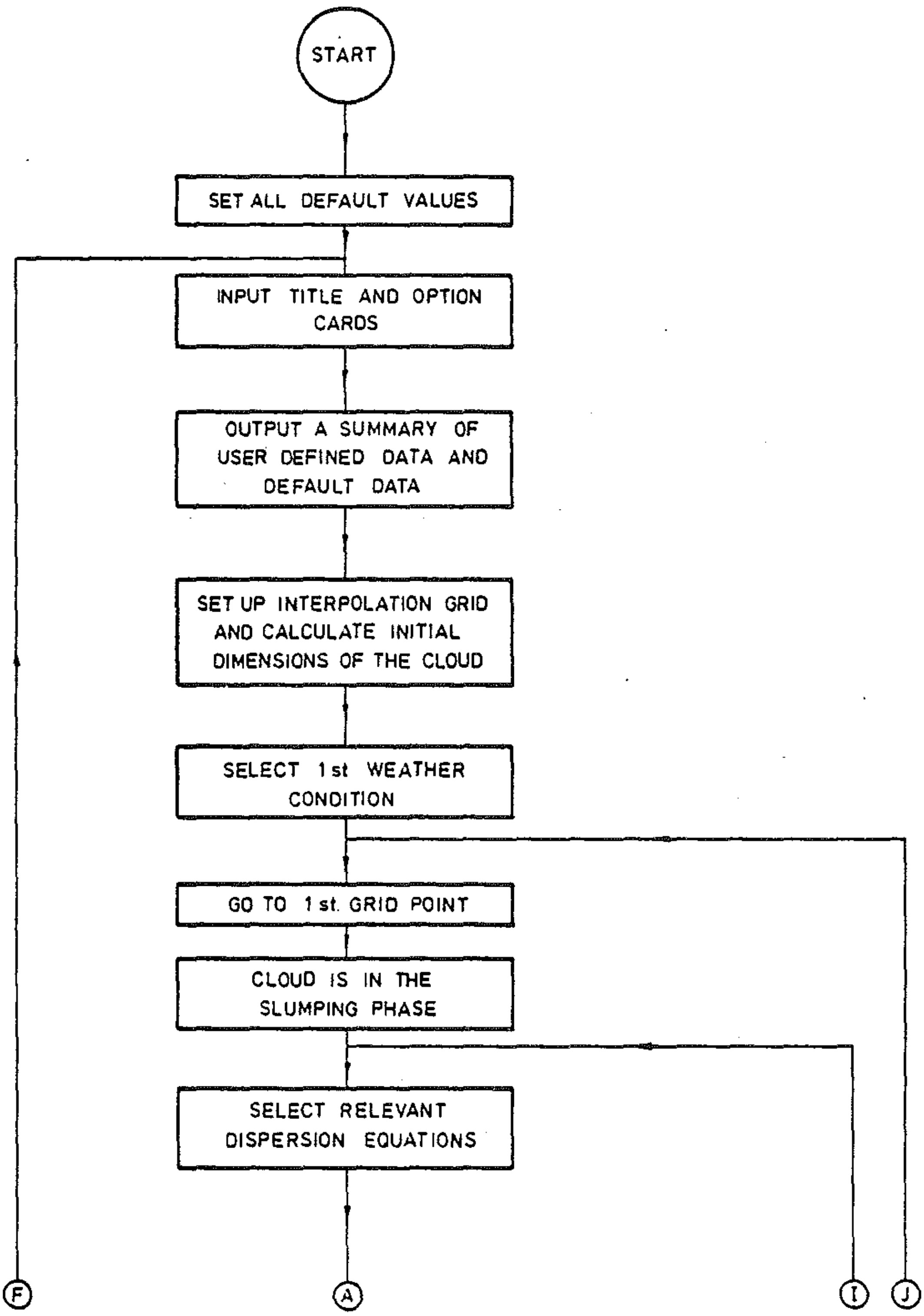
Meteorological data given in Table 1 are used. A 12 sector population distribution is assumed.

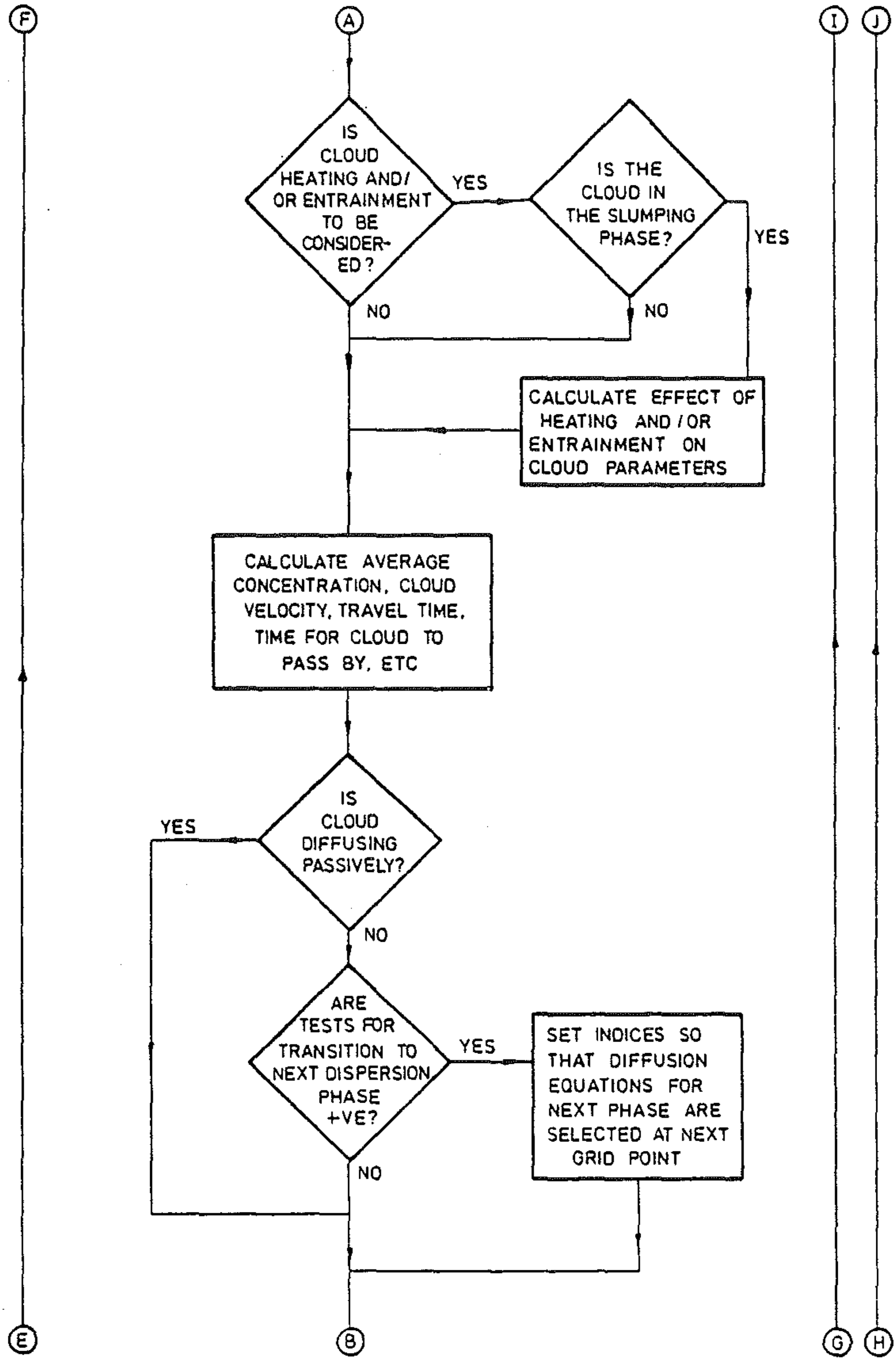
7. ACKNOWLEDGEMENTS

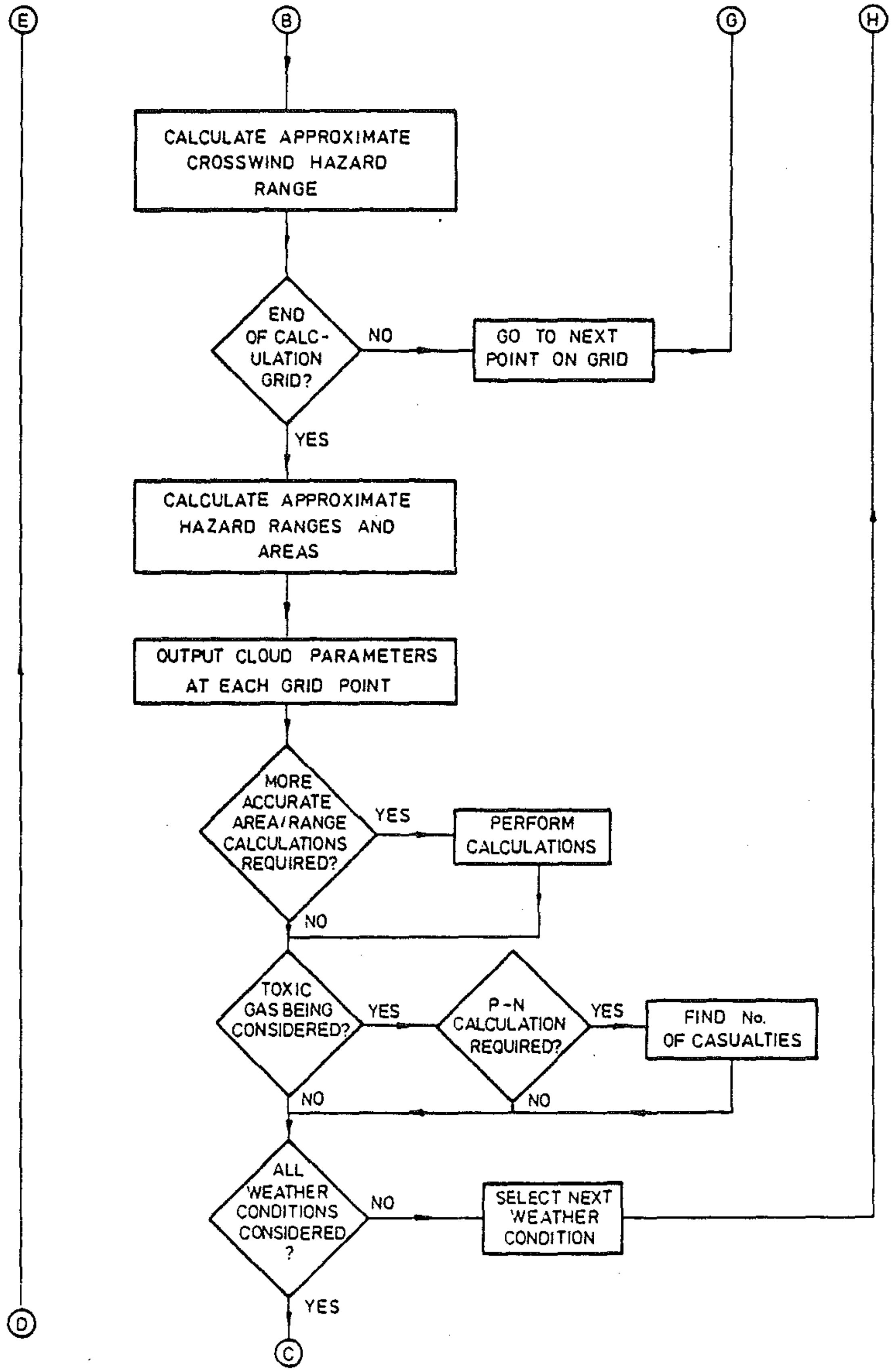
Several people have kindly granted permission for photographs and diagrams to be reproduced. These are the Dutch Directoraat-Generaal Van De Arbeid of the Ministerie Van Sociale Zaken (who provided the colour photographs reproduced in Fig. 1); the Health and Safety Executive, in the person of Dr A. F. Roberts who gave permission for the reproduction of photographs of the Porton experiments; Mr Gene McMullen of the City of Houston Health Department, who gave permission for the reproduction of Fig. 5; Mr Carroll S. Grevemberg of 3601 Allen Parkway, Houston, Texas, who took the photograph appearing as Fig. 4; and Mr A. R. Edwards of SRD, from whose work Fig. 7 was taken.

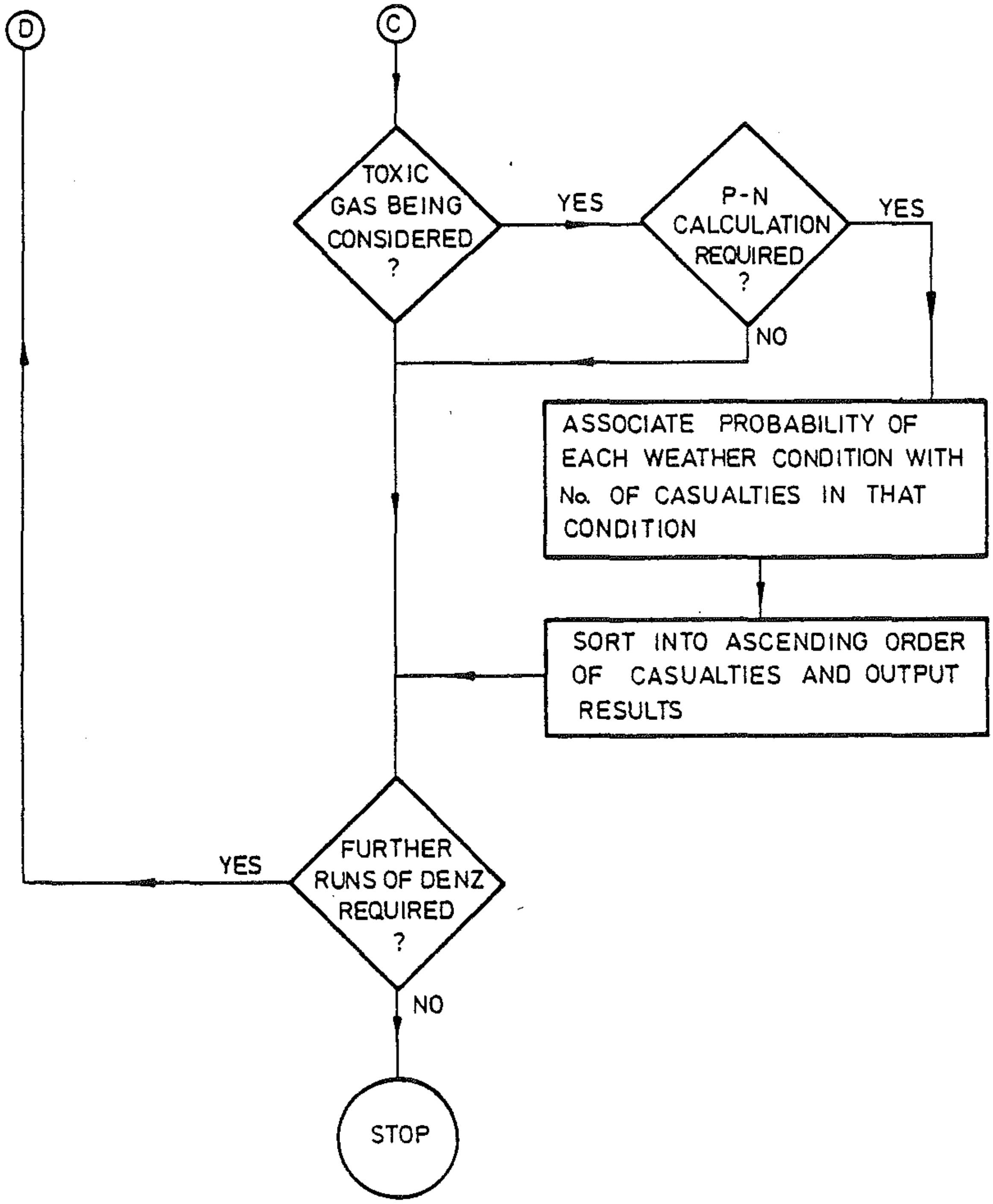
The authors have benefited from discussions with many people among whom are Dr R. F. Griffiths of the Pollution Research Unit, UMIST, and Dr J. C. R. Hunt and colleagues at DAMTP, Cambridge.

8. APPENDIX 1 - FLOW CHART FOR DENZ




F
A
I
J
IS CLOUD HEATING AND/ OR ENTRAINMENT TO BE CONSIDER-ED?
YES
IS THE CLOUD IN THE SLUMPING PHASE?
YES
NO
NO
CALCULATE EFFECT OF HEATING AND/OR ENTRAINMENT ON CLOUD PARAMETERS
CALCULATE AVERAGE CONCENTRATION, CLOUD VELOCITY, TRAVEL TIME, TIME FOR CLOUD TO PASS BY, ETC
IS CLOUD DIFFUSING PASSIVELY?
YES
NO
ARE TESTS FOR TRANSITION TO NEXT DISPERSION PHASE +VE?
YES
SET INDICES SO THAT DIFFUSION EQUATIONS FOR NEXT PHASE ARE SELECTED AT NEXT GRID POINT
NO
E
B
G
H


E
B
G
H
CALCULATE APPROXIMATE CROSSWIND HAZARD RANGE
END OF CALC-ULATION GRID?
NO
GO TO NEXT POINT ON GRID
YES
CALCULATE APPROXIMATE HAZARD RANGES AND AREAS
OUTPUT CLOUD PARAMETERS AT EACH GRID POINT
MORE ACCURATE AREA/RANGE CALCULATIONS REQUIRED?
YES
PERFORM CALCULATIONS
NO
TOXIC GAS BEING CONSIDERED?
YES
P-N CALCULATION REQUIRED?
YES
FIND No. OF CASUALTIES
NO
NO
ALL WEATHER CONDITIONS CONSIDERED ?
NO
SELECT NEXT WEATHER CONDITION
YES
D
C


D
C
TOXIC GAS BEING CONSIDERED ?
YES
P-N CALCULATION REQUIRED ?
YES
NO
ASSOCIATE PROBABILITY OF EACH WEATHER CONDITION WITH No. OF CASUALTIES IN THAT CONDITION
SORT INTO ASCENDING ORDER OF CASUALTIES AND OUTPUT RESULTS
YES
FURTHER RUNS OF DENZ REQUIRED ?
NO
STOP

9. APPENDIX 2

Program structure

9.1 Program language

DENZ is written in FORTRAN for the ICL 2980 computer at Risley.

The input instructions given in Section 6 have been written for users submitting data via cards; however, data may also be input via VDU's or other devices provided that they are presented to the program in the fixed format notation described in Section 6.

9.2 Program size

The code requires about 40 kb and the data a further 70 kb of store, depending to some extent on the calculations to be performed. DENZ requires no disc files or magnetic tapes and has no overlay.

10. APPENDIX 3

Summary of notation

Symbol	Meaning	Units
a	Area of base of 'puff'	m^2
a'	Area of hole in pressurised container	m^2
A_h	Hazard area	m^2
A_s	Area of liquid surface in vessel containing liquified gas	m^2
C_p	Specific heat of mixture at temperature T	$J\,kg^{-1}\,K^{-1}$
C_a	Specific heat of air at temperature T_a	$J\,kg^{-1}\,K^{-1}$
C_g	Specific heat of flammable or toxic gas at temperature T_a	$J\,kg^{-1}\,K^{-1}$
C^*	Coefficient in parametrization of σ_y, Equation (19)	$J\,kg^{-1}\,K^{-1}$
$\bar{C}_f(t)$	Average concentration of toxic vapour required to cause death in time τ	$kg\,m^{-3}$
$\bar{C}(\tau)$	Calculated average concentration over time τ	$kg\,m^{-3}$
d	Diameter of hole in vessel or of pipe	m
ent	Entrainment criterion index	
f	Subscript denoting quantities evaluated at the film temperature	
f_a	Airborne liquid fraction	
f_r	Friction factor, Equation (8)	
g	Acceleration due to gravity	ms^{-2}
h	Height of 'puff'	m
h_c	Height at termination of slumping	m
h_o	Initial height of 'puff'	m
h_t	Height of 'puff' at transition to passivity	m
int	Interval in lnx for calculational grid	
k	Von Karman's constant (~ 0·4)	
K'	Thermal conductivity of 'puff'	$Wm^{-1}\,K^{-1}$
K	Proportionality constant in Van Ulden's formula (Equation (2))	
l	Length of pipe	m
l_s	Turbulence length scale	m
L	Typical dimension of cloud	m
L_f	Lower flammable limit of an explosive gas	kgm^{-3}
m_a	Mass of air in 'puff'	kg
m_{ao}	Mass of air initially in 'puff'	kg
m_g	Mass of toxic or flammable gas in 'puff'	kg
nhaz	Number of hazard levels	
ntype	Index defining type of hazard	
N	Number of people at risk	

Symbol	Meaning	Units
n_t	Number of times for which concentration/exposure time pairs are given as input	
n_r	Number of radii in population distribution	
n_s	Number of sectors	
n_i	Number of velocity subdivisions chosen for weather category i	
$p(j, i, \bar{u}_W)$	Probability that wind will blow into sector j with windspeed $\bar{u}_W$ (10) in weather category i	
P_c	Conditional probability	
Q_c	Rate of cloud heating by the ground	Wm^{-2}
r_d	Maximum radius of interest in the calculation	m
r_i, r_i'	Radii used in defining the population distribution	m
R	Radius of the 'puff'	m
R_o	Initial radius of 'puff'	m
Ri	Richardson number	
R_t	Radius of 'puff' when transition to passivity takes place	m
t	Time after slumping begins	s
t (x)	Time taken for 'puff' centre to reach point x	s
T	Temperature of 'puff'	K
T_o	Initial temperature of 'puff'	K
T_a	Temperature of the atmosphere	K
T_f	Film temperature $= (T_a + T)/2$	K
T_g	Temperature of the ground	K
ΔT_g	$T_g - T$	K
ΔT_a	$T_a - T$	K
$\bar{u}, \bar{u}(t)$	Velocity of 'puff'	ms^{-1}
$\bar{u}_W, \bar{u}_W(10)$	Mean windspeed at a height of 10m	ms^{-1}
u_*	Friction velocity	ms^{-1}
U_e	Entrainment velocity	ms^{-1}
U_l	Longitudinal turbulence velocity	ms^{-1}
V	Volume of 'puff'	m^3
V_o	Initial volume of 'puff'	m^3
V_r	Local velocity difference	ms^{-1}
x	Distance downwind	m
x_t	Distance at which transition to passivity occurs	m
x_h	Hazard range	m
x_j	Position of j^{th} grid point	m
x (t)	Position of centre of 'puff' at time t	m

Symbol	Meaning	Units
y	Distance across the wind	m
y_j	Half crosswind extent of hazardous 'puff' at j^{th} grid point	m
z	Height about the ground	m
z_r	Height of reference wind	m
Z_o	Meteorological roughness length	m
Z	Quantity defined in Equation (5)	
α	Coefficient of $(\Delta T_g)^{\frac{4}{3}}$ in Equation (6)	
α^*	Empirical constant in formula for edge entrainment, Equation (10)	
α'	Empirical constant in formula for entrainment of air over the 'puffs' top surface	
β	Volumetric coefficient of expansion	$m^3 K^{-1}$
ρ	Density of 'puff'	kgm^{-3}
ρ_o	Initial density of 'puff'	kgm^{-3}
ρ_a	Density of air at ambient temperature	kgm^{-3}
ρ_g	Density of toxic or explosive gas at ambient temperature	kgm^{-3}
$\Delta\rho$	$\rho - \rho_a$	kgm^{-3}
$\sigma_x, \sigma_x (x)$	Longitudinal standard deviation in Gaussian formula	m
$\sigma_y, \sigma_y (x)$	Lateral standard deviation in Gaussian formula	m
$\sigma_z, \sigma_z (x)$	Vertical standard deviation in Gaussian formula	m
$\sigma_{xt}, \sigma_{yt}, \sigma_{zt}$	Values of $\sigma_x, \sigma_y, \sigma_z$ at transition to passivity	m
$\sigma_{yh} (x), \sigma_{zh} (x)$	Values of σ_y and σ_z calculated as given by Hosker[38]	m
τ	Exposure time	s
$\tau (x)$	Exposure time at point (x, o, o)	s
$\tau (x, y)$	Exposure time at point (x, y, o)	s
μ	Viscosity of cloud	Pas
$\chi, \chi (x, y, z)$	Airborne concentration (instantaneous or average according to context) at point (x, y, z)	kgm^{-3}

11. APPENDIX 4

List of subprograms

Name	Purpose
AREA	Calculates the approximate downwind area within which potentially hazardous concentrations of gas are found.
CASNO	Determines the number of casualties in each weather condition.
CENCAL	Calculates the average concentration and duration of cloud passage at any point.
DEFOLT	Supplies default values for some control cards.
DENSE	Main program
FANDG	Calculates the vertical standard deviation of the Gaussian distribution.
GRAPH	Interpolates between values of hazardous concentrations/exposure times given by the user, in order to determine hazardous average concentrations for a given duration of cloud passage.
HAIR	Risley library subroutine for solving differential equations.
HAZD	Determines whether or not a given average concentration and duration of cloud passage are hazardous.
HSTAG2	Calculates the effect of heating and/or entrainment during the slumping phase.
ORDER	Calculates cumulative probability curves.
QUAD	Risley library integration subroutine.
READIN	Input routine.
ROOT	Risley library subroutine for finding the roots of an equation.
SIMRAD	Calculates the radius and standard deviation of a non-passively diffusing cloud.
SRTDM	Risley library subroutine for sorting numbers into descending order of magnitude.
STAGE2	Calculates cloud parameters during Stage 2 of the simple dispersion model.
STAGE3	Calculates cloud parameters during Stage 3 of the simple dispersion model.
STAGE4	Calculates parameters of a passively diffusing cloud.
TERP	Performs logarithmic interpolations.
TRANS	Calculates the transition point between Stages 3 and 4 of the simple dispersion model.
XAREA	Performs an accurate calculation of hazard areas and ranges.

12. APPENDIX 5

Examples

The user of DENZ has such a wide choice of input and output that it is not practicable to give examples of them all. The following examples are, therefore, provided to illustrate just two of the possible uses of the program.

12.1 Example one

The input required for a series of runs to investigate the effect of various assumptions about the dispersion of a 'puff' release of 40 Te of ammonia is shown on Table 3. The parameters used are as follows:

(i) *Run 1:* One hazard level with a concentration vs. exposure time curve expressed as four values of hazardous concentration (7×10^{-3} to 5×10^{-4} kg m^{-3}) and four corresponding exposure times (300 to 3,600 seconds).

A hypothetical population distribution consisting of two sectors sub-divided into ten radii (50, 100, 150, 200, 300, 400 ... 800 metres) with one person at each distance in each sector.

Hypothetical meteorological data specifying two velocity subdivisions (3 ms^{-1} and 9 ms^{-1}) in Pasquill stability Category D, and one (2 ms^{-1}) in Category F. The probability of occurrence of each weather condition in each sector of the population distribution is assumed to be the same (values given as input will be normalised by DENZ). Output is required for all weather conditions.

40 Te of gas is assumed to be mixed with 800 Te of air at a density of 1·2 kgm^{-3}, in order to form a source cylinder of density 1·42 Kgm^{-3} at 240 k.

The simple 4-stage model is to be used and area/range calculations are required.

Default values are taken for all other parameters.

(ii) *Run 2:* As Run 1 except that the Cox and Roe model for entrainment of air through the top of the cloud and the heating effect of the entrained air are to be considered.

(iii) *Run 3:* As Run 1 except that heating of the cloud by the ground is to be considered.

(iv) *Run 4:* As Run 1 except that the Cox and Roe model for entrainment of air through the top of the cloud and the heating effect of both the entrained air and the ground are to be considered. The ground temperature is arbitrarily taken to be 293 k and 295 k in stability categories D and F, respectively.

The predicted growth in the radius of the air-ammonia cloud during the slumping phase is shown on Fig. 12. It is apparent that a much broader plume than that indicated by passive diffusion is formed, implying that the region within which potentially hazardous concentrations of ammonia occur is broader than a similar region for a passively diffusing gas of comparable toxicity.

Further discussion of the dispersion of ammonia may be found in Reference 32.

12.2 Example two

The input required for a run to predict the region within which the LFL (~ 5% by volume) is exceeded when 25,000 m^3 of LNG is spilled onto water is shown on Table 4. The principle features of this example are:

(i) It is assumed that as the LNG pool boils it forms a flat cylinder of pure, cold methane.

(ii) The initial radius of the cloud is equal to the estimated maximum liquid pool radius.

(iii) The effect of entrainment through the upper surface and heating of the cloud by the water are to be considered. The air and water temperatures are taken to be 293 k and 283 k, respectively.

(iv) Output is required for all default weather conditions.

This example is presented in view of the publication by Havens[43] containing a review of methods for predicting the hazard range for a spill of 25,000 m^3 of LNG onto water, in which he shows that calculated distances to the LFL in neutral conditions vary from ~ 1 mile to ~ 5 miles, and in stable conditions from ~ 11 miles to ~ 50 miles. The corresponding downwind distances predicted by DENZ are ~ 3 km in Pasquill stability Category D, windspeed 3 ms^{-1}, and ~ 11 km in Category F, windspeed 2 ms^{-1}.

The results from some of the models reviewed by Havens are presented for neutral conditions only; however, since 'the results obtained are not affected strongly by the specification of different atmospheric stability conditions'[43] for at least one model, it may be argued that the lower end of the hazard range given in stable conditions should be extended downwards to include some of the results given for neutral conditions. Havens also expresses reservations concerning the modelling required to produced hazard ranges of several tens of miles. Thus, although the results from DENZ tend towards the lower end of the hazard ranges given by Havens and noting that there is considerable uncertainty about the choice of many modelling parameters – particularly those affecting entrainment and cloud heating – it would seem that the predictions made by DENZ are not inconsistent with those of other models.

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TABLE 1

Default meteorological data

Pasquill stability category	Windspeed m/s	Probability of wind blowing into each sector
A	1·5	$1{\cdot}67 \times 10^{-3}$
B	3·0	$5{\cdot}83 \times 10^{-3}$
C	3·0	$1{\cdot}25 \times 10^{-2}$
D	6·0	$2{\cdot}67 \times 10^{-2}$
	3·0	$2{\cdot}67 \times 10^{-2}$
E	3·0	$5{\cdot}0 \times 10^{-3}$
F	2·0	$5{\cdot}0 \times 10^{-3}$

TABLE 2

Index of control cards

Name of card	Comments	Card number
AIR+	Initial mass and density of air	6.2.1
ALL	Output for all weather conditions	6.3.1
AREA	Base area of cloud	6.3.2
CONTINUE	Another run required	6.4.1
CUT_OFF	Cut-off height for slumping	6.3.3
END+	End of a run	6.4.2
ENTRAIN	Entrainment criterion index	6.3.4
F-NLINES	Probability/no. of casualty calculations required	6.3.5
GAS+	Initial mass and density of released material	6.2.2
HAZARD+	Information on nature of the hazard	6.2.3
HEAT	Cloud heating calculations required	6.3.6
HEIGHT	Height at which input wind speed measured	6.3.7
RANGE	Area/range calculations required	6.3.8
ROUGHNESS	Surface roughness length	6.3.9
SITE	Population data	6.3.10
STAGE_3	Density difference determining termination of stage 3	6.3.11
VAN_ULDEN	Constant in Van Ulden's formula	6.3.12
WEATHER	Meteorological data	6.3.13

+ Compulsory control cards – no default value

7090 PUNCHING FORM

PROBLEM EXAMPLE ONE

CODER | DATE | PAGE 1 OF 2

Ø = Zero

```
****          TOXIC RELEASE
****          4ØTE OF AMMONIA

HAZARD     1.ØØØE ØØ 1.ØØØE ØØ
  4
 7.ØØØE-Ø3 3.5ØØE-Ø3 1.2ØØE-Ø3 5.ØØØE-Ø4
 3.ØØØE Ø2 9.ØØØE Ø2 1.8ØØE Ø3 3.6ØØE Ø3
SITE       1.ØØØE Ø1 2.ØØØE ØØ
 5.ØØØE Ø1 1.ØØØE Ø2 1.5ØØE Ø2 2.ØØØE Ø2 3.ØØØE Ø2 4.ØØØE Ø2 5.ØØØE Ø2 6.ØØØE Ø2
 7.ØØØE Ø2 8.ØØØE Ø2
 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ
 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ
 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ 1.ØØØE ØØ
WEATHER                                  2.ØØØE ØØ           1.ØØØE ØØ
 3.ØØØE ØØ 9.ØØØE ØØ
 2.ØØØE ØØ
 1.ØØØE ØØ 1.ØØØE ØØ
 1.ØØØE ØØ 1.ØØØE ØØ
 1.ØØØE ØØ 1.ØØØE ØØ
GAS        4.ØØØE Ø4 1.42ØE ØØ 2.4ØØE Ø2
AIR        8.ØØØE Ø5 1.2ØØE ØØ
ENTRAIN    Ø.ØØØE ØØ
ALL
RANGE
END
```

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TABLE 3 : INPUT FOR EXAMPLE ONE

7090 PUNCHING FORM

PROBLEM

CODER | DATE | PAGE 2 OF 2

```
CONTINUE
****          RUN TWO - HEATING BY ENTRAINMENT

ENTRAIN    1.ØØØE ØØ 2.93ØE Ø2 Ø.ØØØE ØØ 5.ØØØE-Ø1
HEAT                 1.Ø11E Ø3 1.846E Ø3 2.93ØE Ø2 7.71ØE-Ø1
END
CONTINUE
****          RUN THREE - HEATING BY THE GROUND

ENTRAIN    Ø.ØØØE ØØ
HEAT       1.957E ØØ 1.Ø11E Ø3 1.846E Ø3 2.93ØE Ø2 7.71ØE-Ø1
END
CONTINUE
****          RUN FOUR - HEATING BY ENTRAINMENT AND BY THE GROUND

ENTRAIN    1.ØØØE ØØ 2.93ØE Ø2 Ø.ØØØE ØØ 5.ØØØE-Ø1
HEAT       1.957E ØØ 1.Ø11E Ø3 1.846E Ø3 2.93ØE Ø2 7.71ØE-Ø1           1.ØØØE ØØ
 2.93ØE Ø2 2.93ØE Ø2
 2.95ØE Ø2
END
END
```

TPG 3014(REV.9/65)

TABLE 3 (Continued)

7090 PUNCHING FORM

PROBLEM EXAMPLE TWO

CODER | DATE | PAGE 1 OF 1

Ø = Zero

```
++++       RELEASE OF FLAMMABLE MATERIAL
++++       25ØØØM**3 OF LNG SPILLED ONTO WATER

AIR        Ø.ØØØE ØØ 1.2ØØE ØØ
GAS        1.Ø57E Ø7 1.766E ØØ 1.1Ø1E Ø2
HAZARD     1.ØØØE ØØ 2.ØØØE ØØ
 3.734E-Ø2
ENTRAIN    1.ØØØE ØØ 2.93ØE Ø2 Ø.ØØØE ØØ 5.ØØØE-Ø1
ALL
HEAT       2.Ø81E ØØ 9.9ØØE Ø2 2.219E Ø3 2.93ØE Ø2 6.679E-Ø1           1.ØØØE ØØ
 2.83ØE Ø2
 2.83ØE Ø2
 2.83ØE Ø2
 2.83ØE Ø2 2.83ØE Ø2
 2.83ØE Ø2
 2.83ØE Ø2
AREA       4.6Ø8E Ø5
RANGE
END
END
```

TRC 5014(REV.9/65)

TABLE 4 : INPUT FOR EXAMPLE TWO

(a)

(b)

FIGURE 1 The release of 1 Te of Freon−12 by pouring refrigerated liquid onto water.

(a) An approximately cylindrical cloud forms within the first few seconds.

(b) The puff subsequently collapses under the influence of gravity.

(c) Slumping continues until the cloud has a height of only a fraction of a metre.

(c)

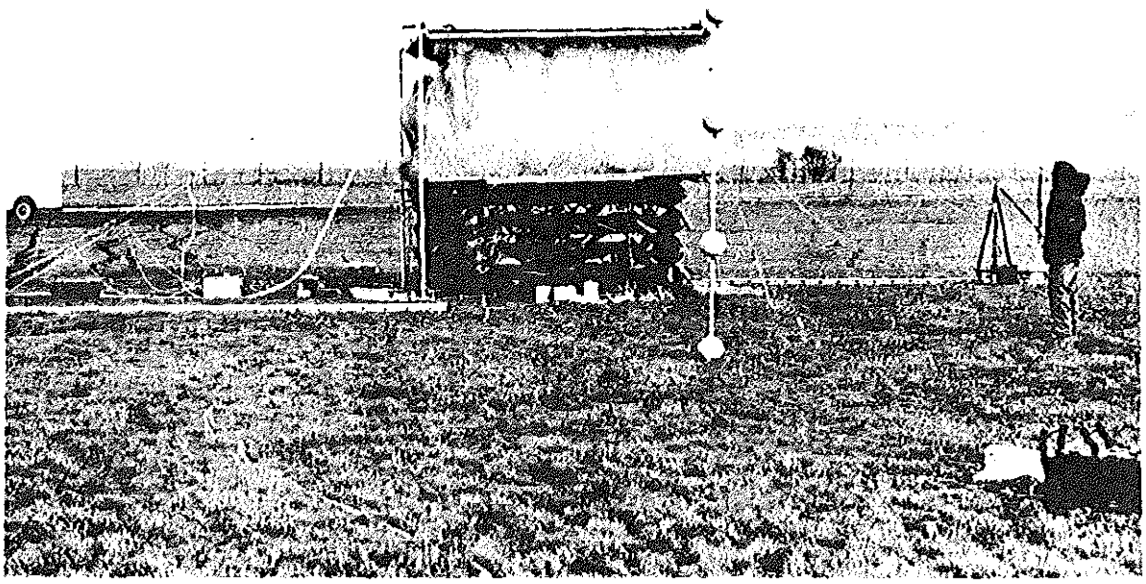

FIGURE 2

The source 'tent' for the releases of Freon-12 at Porton, as it begins to collapse. The gas is made visible with a smoke grenade.

FIGURE 3(a) Collapse of Freon – 12 'puff' when there is little wind.

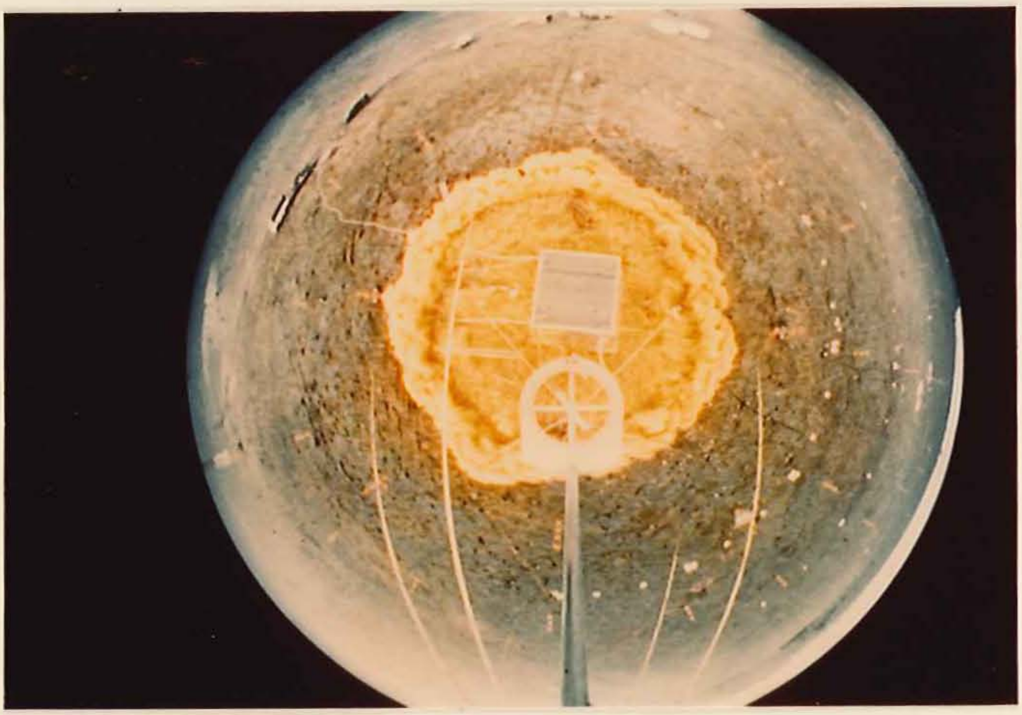

FIGURE 3(b) The same release viewed from above after a few seconds using a 'fisheye' lens. Note the 'flan-case' configuration.

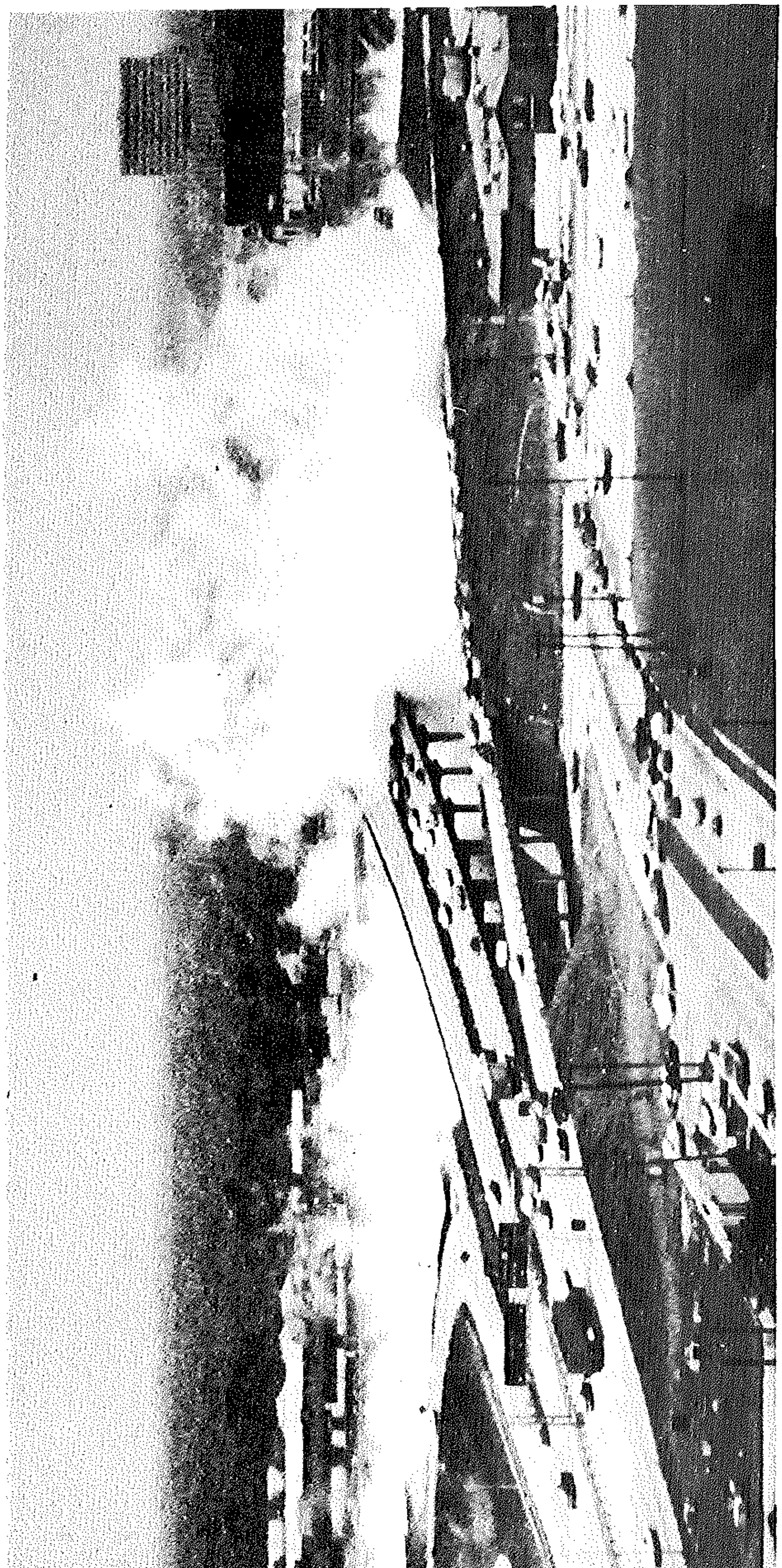

FIGURE 5 Houston; Photographs of grass burnt by the escaping ammonia, taken four days later from a helicopter.

Above: looking eastwards.
Below: looking westwards.

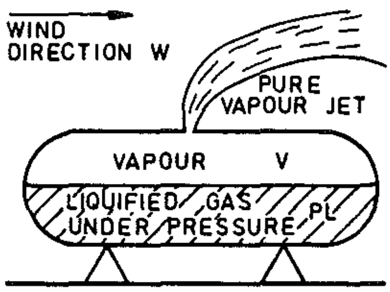

FIG. 6A SMALL HOLE IN VAPOUR SPACE-PRESSURIZED TANK

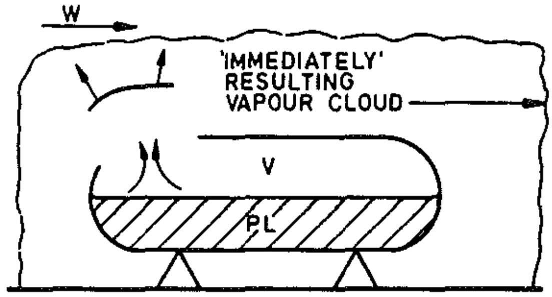

FIG. 6B CATASTROPHIC FAILURE OF PRESSURIZED TANK

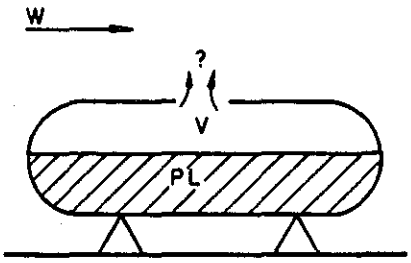

FIG. 6C INTERMEDIATE HOLE IN VAPOUR SPACE-PRESSURIZED TANK

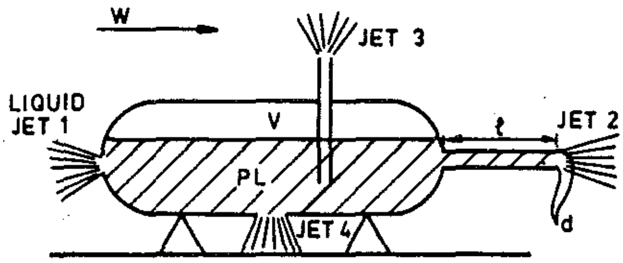

FIG. 6D ESCAPE OF LIQUIFIED GAS FROM A PRESSURIZED TANK

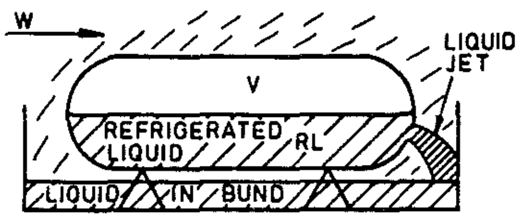

FIG. 6E SPILLAGE OF REFRIGERATED LIQUID INTO BUND

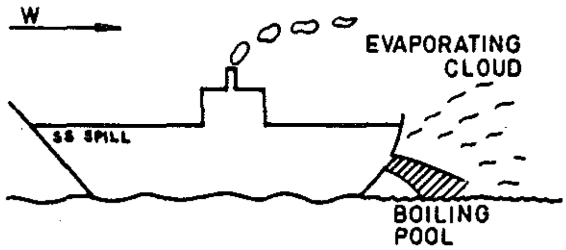

FIG. 6F SPILLAGE OF REFRIGERATED LIQUID ONTO WATER

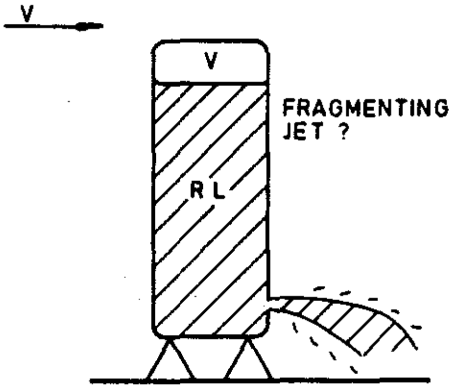

FIG. 6G HIGH VELOCITY FRAGMENTING JET FROM REFRIGERATED CONTAINMENT

FIG. 6 ILLUSTRATION OF SOME CONCEIVABLE RELEASE MECHANISMS

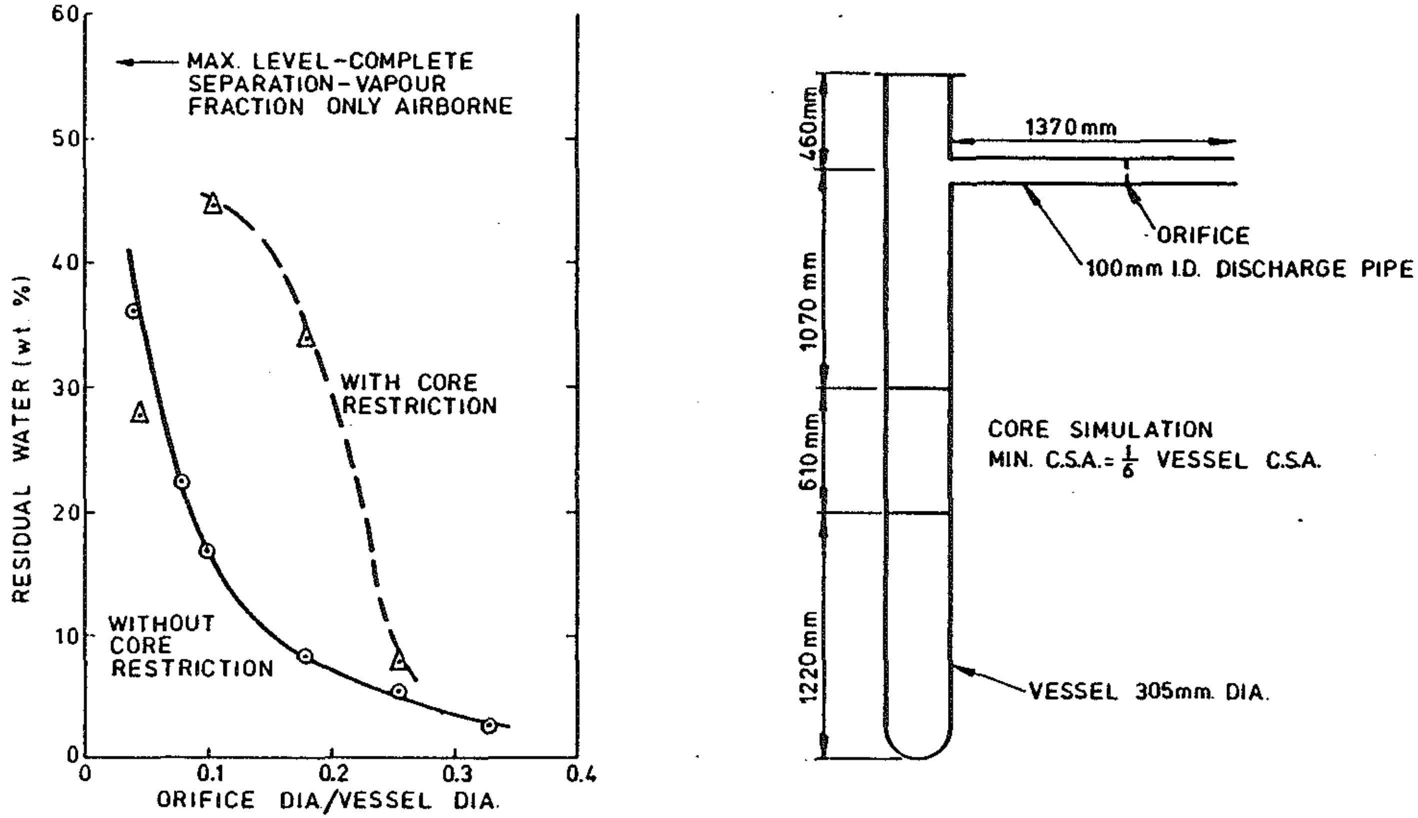

FIG. 7 EFFECT OF INTERNAL RESTRICTION ON WATER REMAINING AFTER BLOWDOWN. INITIAL PRESSURE 160 bar. TEMP. = 272°C (FROM REF. 23)

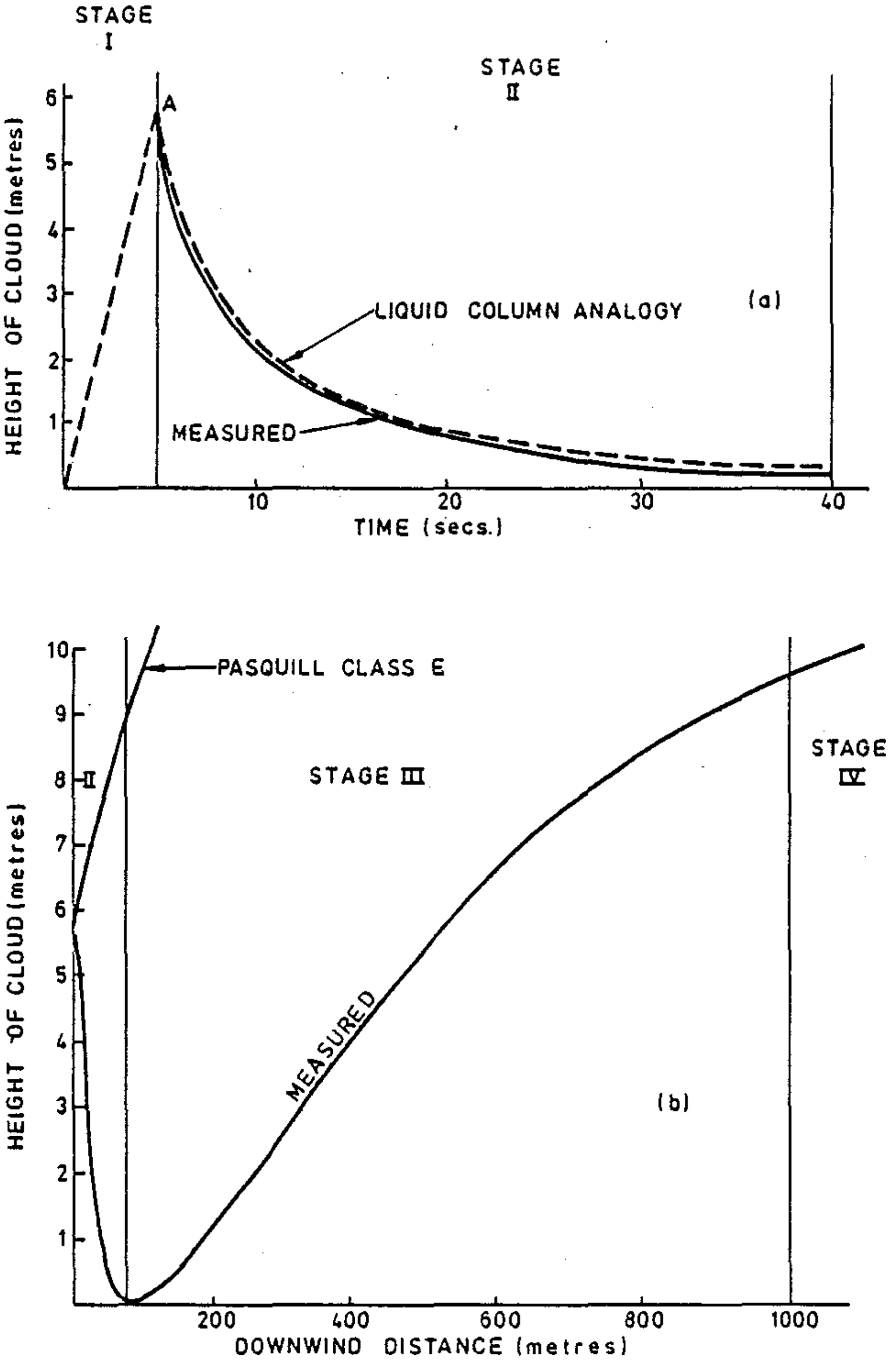

FIG.8 GROWTH OF HEIGHT IN VAN ULDEN'S EXPERIMENT

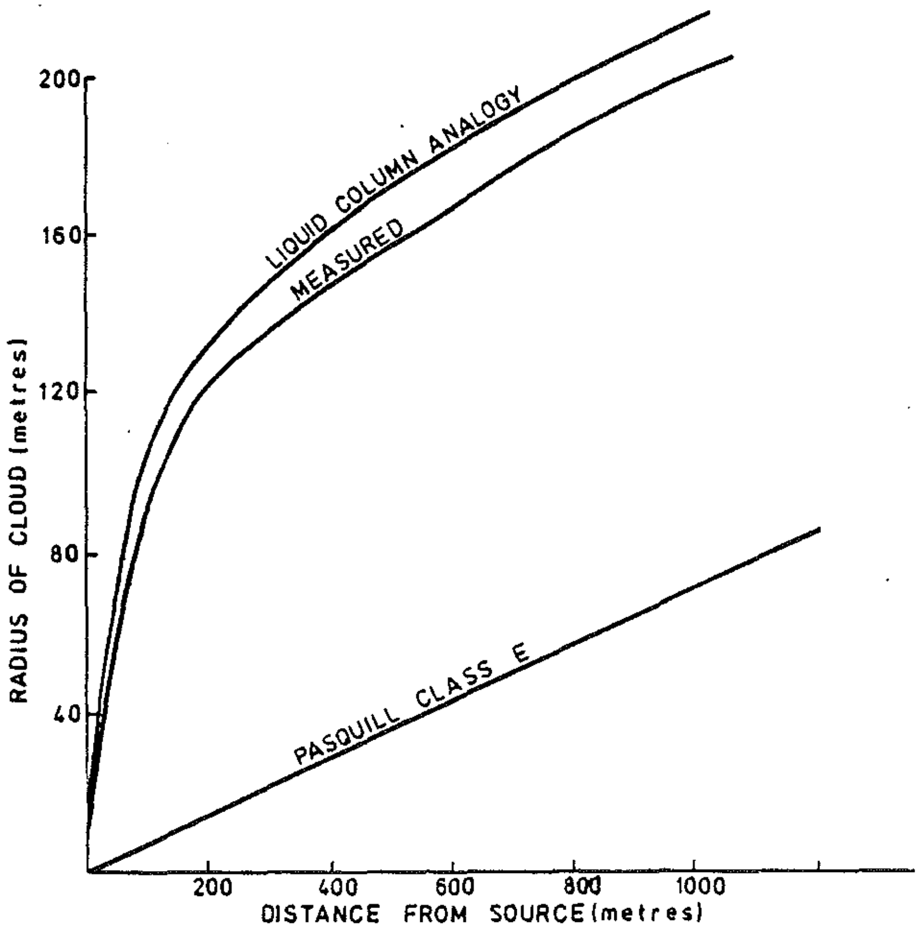

FIG. 9 RADIUS OF CLOUD IN VAN ULDEN'S EXPERIMENT

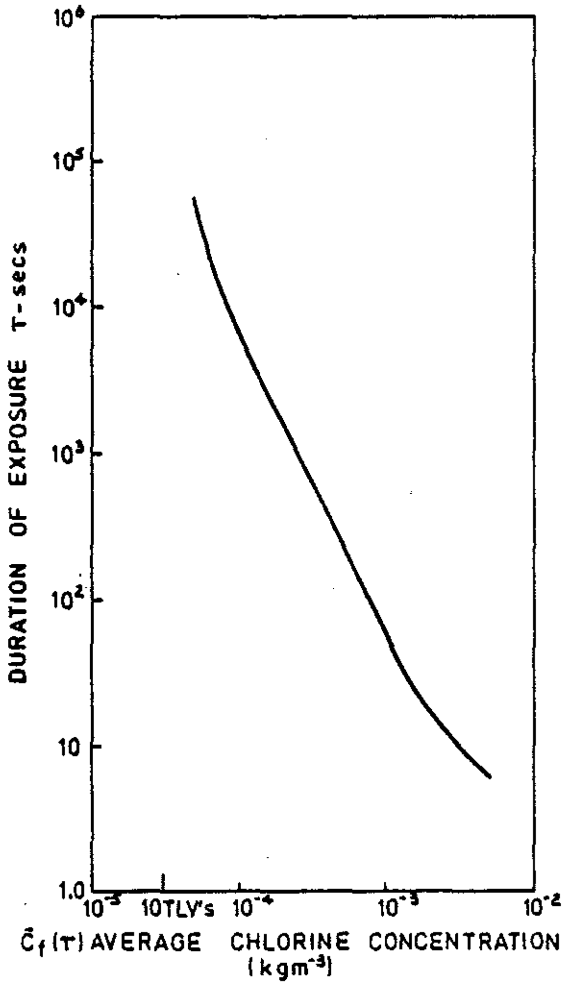

FIG. 10 AVERAGE CONCENTRATION AND LETHAL EXPOSURE TIMES FOR CHLORINE

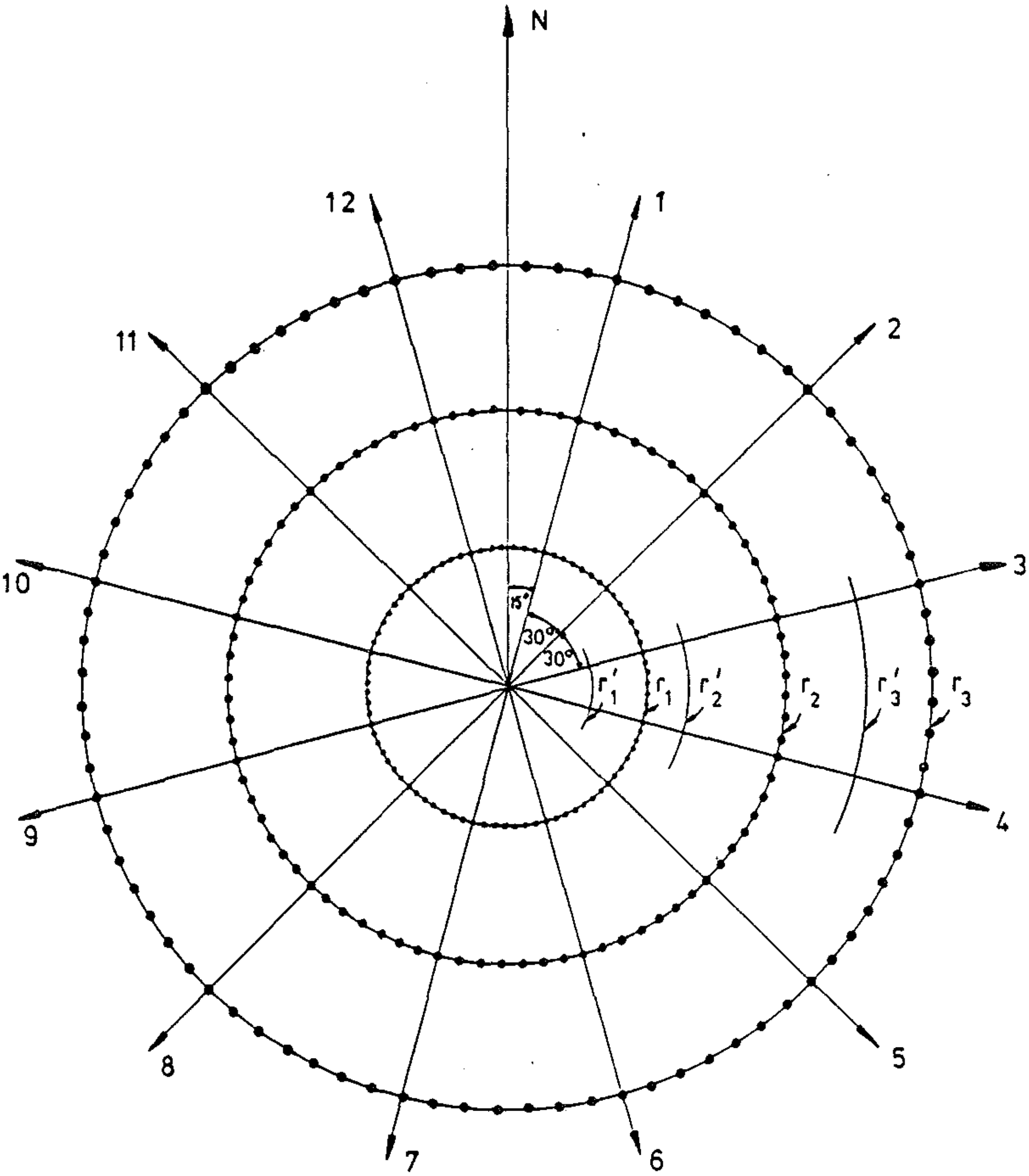

FIG. 11 DEFINITION OF WIND DIRECTIONS AND POPULATION DISTRIBUTIONS

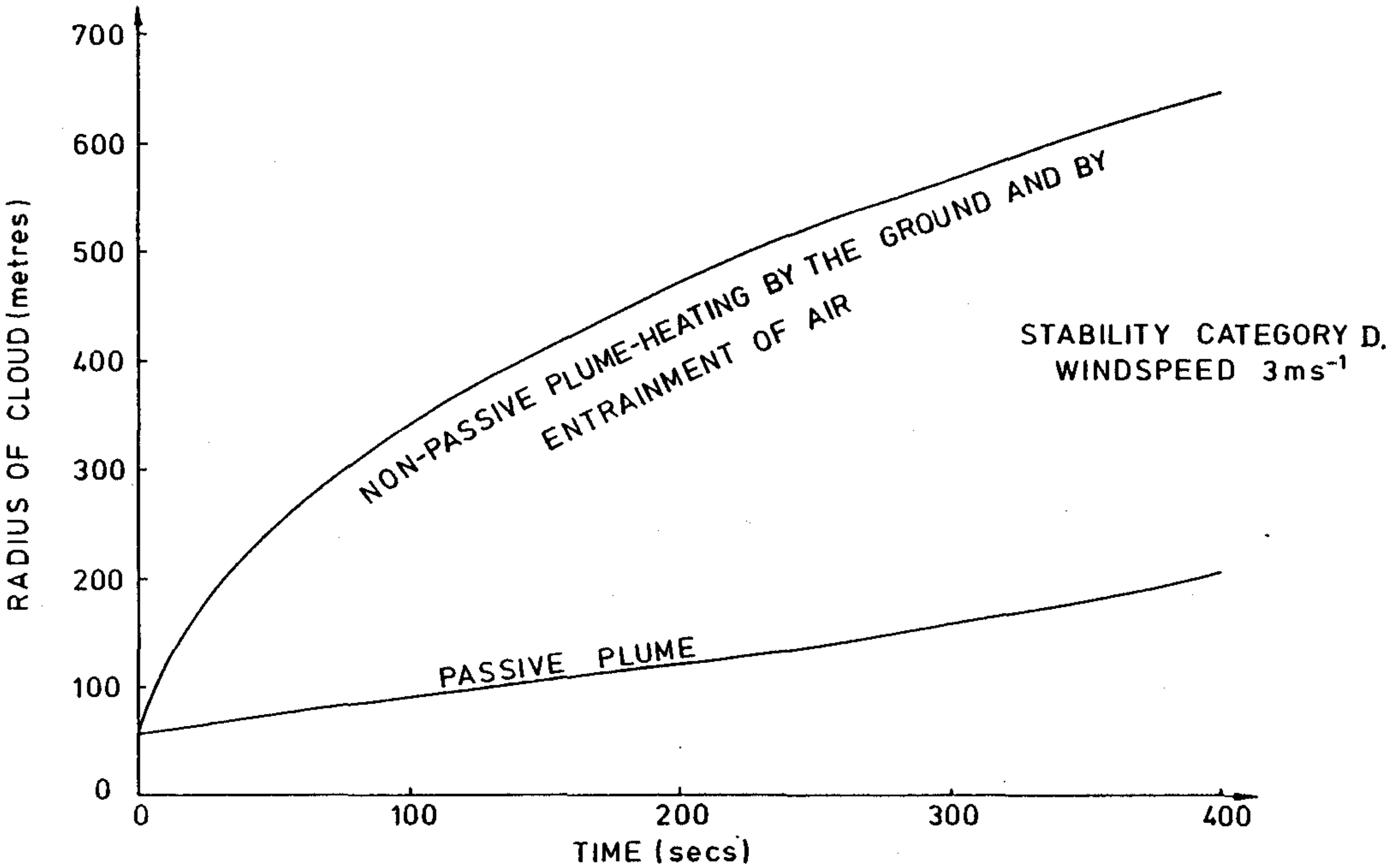

FIG.12 GROWTH IN RADIUS OF CLOUD DURING SLUMPING PHASE